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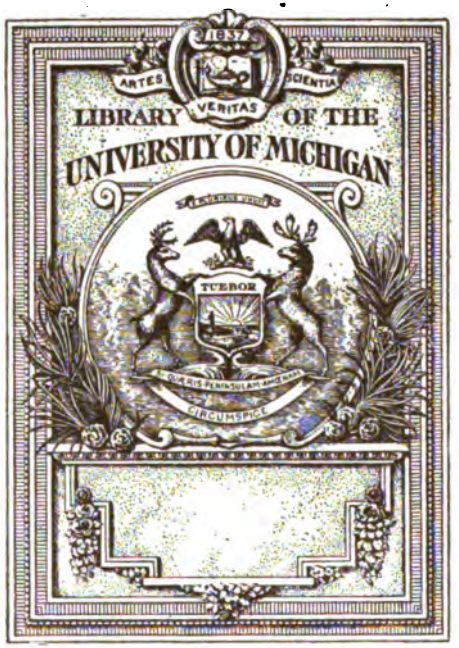
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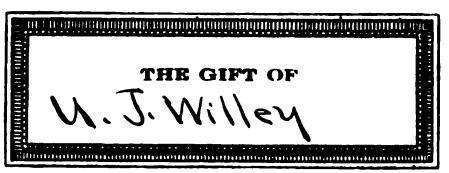
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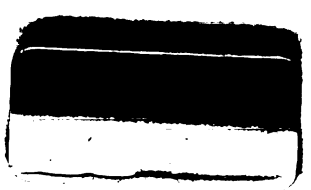

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QUALITATIVE CHEMICAL ANALYSIS OF

INORGANIC SUBSTANCES

ERRATA.

P. 11, 1st column, 8th line from bottom, omit the comma after "great excess."

P. 14, No. 11 heading, insert a comma and space before "$Cd(OH)_2$."

P. 20, No. 1, for "$(NH_4)_4AsS_5$" read "$(NH_4)_4As_2S_5$."

P. 25, 2d column, 6th line, for "FeSO" read "$FeSO_4$."

P. 26, 1st column, 3d line, substitute a comma for the semicolon after "aluminates."

P. 60, 1st column, 8th line, omit the comma after "reagent," also after "NH_4OH."

P. 60, 2d column, 4th line, for "reagent ammonium" read "reagent ammonia."

E, D. C.

CHICAGO

QUALITATIVE CHEMICAL ANALYSIS OF INORGANIC SUBSTANCES

AS PRACTICED IN GEORGETOWN COLLEGE, D. C.

AMERICAN BOOK COMPANY

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PREFACE.

THIS little book may be considered as the outcome of a series of Analytical Tables prepared and printed for the use of his classes by Rev. H. T. B. Tarr, S. J., formerly Professor of Chemistry in Georgetown College, and revised and reprinted for the same use by Rev. John W. Fox, S. J. These Tables, originally intended merely as a preliminary step towards a more complete text-book, have been entirely recast and incorporated in the present work, in which they have been supplemented by such explanatory and descriptive notes and working directions as experience has shown to be useful in a course such as is given at Georgetown and in similar institutions throughout the country. Little or no pretense is made to originality, either in matter or in method, but the book has been compiled chiefly from the standard text-books of Fresenius, Prescott and Johnson, the new Watts's Dictionary of Chemistry, edited by Morley and Muir, and its companion work, the Dictionary of Applied Chemistry, by Thorpe. Only those facts have been selected which are indispensable in a course such as the one for which the book is intended. For the rest, the student is expected to consult the larger works mentioned, to which in many cases references are given.

GEORGETOWN COLLEGE, D. C.,
June, 1894.

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INTRODUCTION.

QUALITATIVE ANALYSIS is that branch of chemistry which treats of the detection of the chemical elements and their compounds. It employs two methods: 1st, the *Dry Way;* 2d, the *Wet Way.* In either case, any *known* substance which is used to effect a change is called a *reagent;* the change effected is called a *reaction.* In the Dry Way, reactions are dependent on *volatilization* and *changes effected by heat;* in the Wet Way, reactions are brought about by means of *solutions.* A reagent which affects several substances at once is called a *general* reagent; if only one substance is affected, the reagent is a *special* one.

The changes brought about depend on two universal laws, known as the Laws of Berthollet:

1. *When solutions of different substances are mixed, and a substance insoluble under existing circumstances can be formed, it is formed and separates.*

2. *When a substance volatile under existing circumstances can be formed, it is formed and escapes.*

The insoluble substance that separates in accordance with the first law is called a *precipitate;* the liquid that is decanted or filtered from it is called a *filtrate.*

As is evident, precipitation may result from either of two conditions: (1) from a change of the substance in solution; (2) from a change of the menstruum. An example of the first kind is had when to a solution of barium nitrate in water, sulphuric acid is added; barium sulphate is formed, and, being insoluble in water, is precipitated. An example of the second kind is had when to a solution of the same substance, barium nitrate, concentrated nitric acid is added; evidently no change takes place in the substance in solution, but the menstruum is changed from water to nitric acid, in which barium nitrate is insoluble; hence it is precipitated unchanged.

The study of Qualitative Analysis is universally admitted to be among the very best means of acquiring a knowledge of the facts and methods of chemistry, but it is of value only when pursued intelligently. This requires an accurate knowledge of the properties of the elements and their compounds, in particular of their solubilities and of the conditions under which precipitates will form, and also a familiarity with the general principles of the science of chemistry. A mere mechanical acquaintance with a working scheme for separating the different bases and acids is at best but a questionable accomplishment, and certainly not worthy of a place in any system of

mental discipline. The student should never be permitted to pass from one step to another without understanding thoroughly what he has just done, and what he should expect to take place in the next step under normal conditions. Causes of error should be sought out, and remedies applied.

The following method is suggested, as having been successfully used at Georgetown for many years. The study of the bases is first taken up, and the student made to familiarize himself, by lectures, recitations, and laboratory work, with the properties of the separate Groups. Exercises such as are given at the end of Remsen's Chemistry are gone through in the laboratory, results are compared in the recitation room, and the students make out their own schemes of analysis. The instructor next explains the working scheme in the book, and goes through the manipulation before the class, after which a known solution is given, containing all the bases of the Group. A recitation follows, and two or three unknown solutions are analyzed. The following Group is then taken up, in the same order, and finally general unknown solutions are given, until the instructor is entirely satisfied with the work done. Acid analysis and the preliminary examination are given in about the same way, and the rest of the course is spent in work upon solids of various kinds,—mixtures of salts, graded from the simplest to the more complex, minerals, alloys, etc.

In the laboratory, the most exact order and neatness are indispensable to successful work. The apparatus must be kept in thorough repair, and must never be put away uncleaned. The reagents must never be left exposed to the air, and stoppers should never be placed on the table. Every reagent should be added cautiously, and in quantity just sufficient to insure the desired effect. It is essential, also, that a concise and accurate record be kept, stating the reactions that occur, under what conditions they take place, and what conclusions may be drawn from them. This record must be written as the work is being done, and must not be delayed, because it is useful only inasmuch as it recalls the phenomena noticed in the actual course of any particular analysis.

PART I.—BASIC ANALYSIS.

GROUPING OF THE BASES.

For purposes of analysis, the bases are divided into five Groups, according to their behavior with certain reagents, as follows:

Group V contains those metals whose chlorides are insoluble in water, and which consequently are precipitated by HCl; viz., Pb, Ag, Hg_2 (mercury in mercurous combinations).

Group IV contains those bases which are not precipitated by HCl, the reagent of Group V, but are precipitated as sulphides by H_2S, more completely in presence of HCl. It is divided into two subgroups:

A. Sulphides insoluble in $(NH_4)_2S_x$—the yellow sulphide of ammonium,—viz., Hg (in mercuric combinations), (Pb), Bi, Cu, Cd.

B. Sulphides soluble in the above-mentioned reagent; viz., As, Sb, Sn.

Group III contains those metals which are not precipitated by HCl, nor by H_2S in presence of HCl, but are precipitated by $(NH_4)_2S$ from neutral or alkaline solution; viz., Co, Ni, Mn, Zn, Fe, Al, Cr.

Group II contains those metals whose chlorides and sulphides are soluble, but whose carbonates are precipitated by $(NH_4)_2CO_3$ from neutral or alkaline solution; viz., Ba, Sr, Ca. Mg, which is not thrown down by any of the reagents mentioned, when NH_4Cl is present, is also classed in this Group. It is precipitated by Na_2HPO_4.

Group I contains those metals all of whose ordinary salts are soluble, and which, consequently, are not precipitated by any of the usual reagents; viz., NH_4, K, Na, Li.

The following scheme shows the Group separations in tabular form:

TABLE I.—GROUP SEPARATIONS.

To the original solution add **HCl** in slight excess.

V.—Precipitate.
$PbCl_2$ (white)
Hg_2Cl_2 (white)
AgCl (white)

Consult Table II.

Filtrate. Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Co, Ni, Mn, Zn, Fe, Al, Cr, Ba, Sr, Ca, Mg, Na, K, Li, NH_4, besides phosphates and oxalates of Gr. II. Heat to boiling and add H_2S.

IV.—Precipitate.

A. Insoluble in $(NH_4)_2S_x$.
- HgS (black)
- PbS (black)
- Bi_2S_3 (black)
- CuS (black)
- CdS (yellow)

B. Soluble in $(NH_4)_2S_x$.
- As_2S_3 (yellow)
- Sb_2S_3 (orange)
- SnS (brown)
- SnS_2 (yellow)

Consult Tables III and IV.

Filtrate. Co, Ni, Mn, Zn, Fe, Al, Cr, Ba, Sr, Ca, Mg, Na, K, Li, NH_4, besides phosphates, etc., of Gr. II. Add NH_4Cl, NH_4OH, heat to boiling, and add $(NH_4)_2S$.

III.—Precipitate.
- NiS (black)
- CoS (black)
- MnS (flesh color)
- ZnS (white)
- FeS (black)
- $Al_2(OH)_6$ (white)
- $Cr_2(OH)_6$ (pale green)

phosphates and oxalates of Gr. II.

Consult Tables V and VI.

Filtrate. Ba, Sr, Ca, Mg, Na, K, Li, NH_4. Evaporate to remove $(NH_4)_2S$, filter off S, and to filtrate add NH_4Cl, NH_4OH, heat, and add $(NH_4)_2CO_3$.

II.—Precipitate.
- $BaCO_3$ (white)
- $SrCO_3$ (white)
- $CaCO_3$ (white)

Consult Table VII.

I.—Filtrate. Mg, Na, K, Li, NH_4. Add to a portion Na_2HPO_4; a white precipitate, $MgNH_4PO_4$, indicates Mg. Filter, evaporate filtrate to dryness, and test for Na, K, Li, NH_4.

Consult Table VIII.

PROPERTIES OF GROUP V.

SILVER (Ag).—108.

A white metal with high luster, moderately hard, very malleable and ductile; best of the metals as a conductor of heat and electricity. Sp. Gr. 10.55. It is readily soluble in dilute HNO_3, insoluble in HCl and dilute H_2SO_4. Concentrated H_2SO_4 forms Ag_2SO_4, sparingly soluble.

Soluble Compounds.—**Nitrate,** $AgNO_3$, is readily soluble; **Acetate,** $AgC_2H_3O_2$, and **Sulphate,** Ag_2SO_4, sparingly soluble.

Insoluble Compounds.—There are three **Oxides,**—Ag_4O, Ag_2O, Ag_2O_2. The second, Ag_2O, the only one commonly met with, is precipitated as a dark brown powder by KOH or NaOH. It is soluble in HNO_3, $HC_2H_3O_2$, H_2SO_4, NH_4OH, and in solutions of cyanides and thiosulphates.

Chloride, AgCl, white, is completely precipitated by dilute HCl, imperfectly by solutions of metallic chlorides and by concentrated HCl. It dissolves readily in NH_4OH, as an ammonio-silver chloride. From this solution acids reprecipitate AgCl. It is also soluble in solutions of cyanides and thiosulphates. Exposed to light, the precipitate darkens from loss of Cl, and in this condition is not acted on by the ordinary solvents.

Bromide, AgBr, white, inclining to yellow, is precipitated by solutions of bromides. It is slightly soluble in excess of the reagent, less readily than AgCl in NH_4OH, easily in solutions of cyanides and thiosulphates.

Iodide, AgI, pale yellow, precipitated by solutions of iodides; soluble in excess of the reagent as a double salt; *e. g.*, AgIKI. On diluting this solution with water, AgI is again thrown down. AgI is almost entirely insoluble in NH_4OH, but dissolves readily in solutions of cyanides and thiosulphates.

Sulphide, Ag_2S, black, precipitated by H_2S and $(NH_4)_2S$. Soluble in HNO_3.

Carbonate, Ag_2CO_3, white, precipitated by NaOH and KOH, not by NH_4OH. Soluble in HNO_3 and NH_4OH. Boiling changes it to Ag_2O.

Most of the remaining insoluble Ag salts are described in detail in Acid Analysis.

Ag is easily reduced by Zn and many other metals.

LEAD (Pb).—207.

A bluish-white metal, very soft, easily fusible, malleable. Sp. Gr. 11.38. It is soluble in HNO_3; insoluble in HCl and H_2SO_4.

Soluble Compounds.—**Nitrate,** $Pb(NO_3)_2$; **Chlorate,** $Pb(ClO_3)_2$; **Acetate,** $Pb(C_2H_3O_2)_2$.

Insoluble Compounds.—**Oxides,** Pb_2O, PbO, Pb_2O_3, Pb_3O_4, not of importance in analysis. All are converted to

PbO when ignited in air. PbO is soluble in HNO_3 and $HC_2H_3O_2$.

Hydroxide, $Pb(OH)_2$, white, precipitated by NaOH and KOH; soluble in excess of reagent as *plumbite; e. g.*, Na_2PbO_2; soluble also in HNO_3 and $HC_2H_3O_2$. NH_4OH gives basic salts; *e. g.*, from $Pb(NO_3)_2$, $Pb_3O_2OHNO_3$ is formed.

Chloride, $PbCl_2$, white, precipitated by dilute HCl; very sparingly soluble in cold water, but quite freely soluble in hot water.

Bromide, $PbBr_2$, white, precipitated by solutions of bromides; sparingly soluble in hot water, more sparingly in cold; soluble in excess of precipitant.

Iodide, PbI_2, golden yellow crystals, precipitated by solutions of iodides; very sparingly soluble in water; soluble in excess of precipitant, and in moderately concentrated HNO_3.

Sulphide, PbS, brownish-black, precipitated by H_2S and solutions of alkaline sulphides; insoluble in cold dilute acids, in alkalies, and in concentrated H_2SO_4 and HCl; soluble in boiling, moderately dilute HNO_3. (See Explanation of Working Scheme.)

Sulphate, $PbSO_4$, white, precipitated by H_2SO_4 and solutions of sulphates; soluble in KOH and NaOH, and in $NH_4C_2H_3O_2$. (See Explanation of Working Scheme.)

Chromate, $PbCrO_4$, yellow, precipitated by solutions of chromates and dichromates; soluble in KOH and NaOH. (See Explanation of Working Scheme.) See page 11.

MERCURY (Hg).—200.

The only metal liquid at ordinary temperatures; solidifies at −39.5°. Silver-white, high luster. Sp. Gr. 13.6. It is insoluble in HCl and in cold H_2SO_4; soluble in hot H_2SO_4, in HNO_3 and in aqua regia. It forms two classes of compounds: *mercuric*, in which the single atom, Hg, is bivalent; and *mercurous*, in which the double atom, Hg_2, is bivalent. Mercurous compounds alone are considered in this group.

Mercurous Combinations.

Soluble Compounds.—Nitrate, $Hg_2(NO_3)_2$, formed by dissolving the metal in HNO_3, the metal being in excess. In solution it gradually changes to $Hg(NO_3)_2$, unless free Hg be present. On standing, solutions of $Hg_2(NO_3)_2$ gradually deposit a yellow basic salt, soluble in HNO_3.

Sulphate, Hg_2SO_4, and **Acetate,** $Hg_2(C_2H_3O_2)_2$, are sparingly soluble in water, readily soluble in acidulated water.

Insoluble Compounds.—Oxide, Hg_2O, black, precipitated by KOH and NaOH; insoluble in alkalies; soluble in dilute HNO_3 and dilute H_2SO_4, forming mercurous salts.

There is no hydroxide. NH_4OH gives *mercurosammonium* compounds.

Chloride, Hg_2Cl_2, white, precipitated completely by dilute HCl, imperfectly by concentrated HCl and by solutions of chlorides; dissolves slowly in hot concentrated HCl, readily in aqua regia, to $HgCl_2$. NH_4OH changes it to black dimercurosammonium salt, NH_2Hg_2Cl. (See Explanation of Working Scheme.)

Bromide, Hg_2Br_2, yellowish-white, precipitated by solutions of bromides; insoluble in cold dilute HNO_3, slowly soluble in hot HNO_3, soluble in hot concentrated H_2SO_4; decomposed by hot HCl.

Iodide, Hg_2I_2, greenish-yellow, precipitated by soluble iodides; partly soluble in excess of precipitant, and in NH_4OH.

TABLE II.—ANALYSIS OF GROUP V.

Pb, Hg_2, Ag.

1. To the cold original solution add dilute **HCl** in slight excess, filter, and test filtrate again with **HCl.**

2. **Filtrate.** Groups IV—I. Reserve to test for members of these Groups.

3. **Precipitate.** $PbCl_2$, Hg_2Cl_2, AgCl. Wash with cold water, transfer to test tube, digest with **hot water,** and filter.

4. **Solution.** $PbCl_2$ is dissolved in the hot water. Add dilute H_2SO_4 in excess, and let stand. A white precipitate, $PbSO_4$, indicates Pb. Or,
Add H_2S. A black precipitate, PbS, indicates Pb.

5. **Residue.** AgCl, Hg_2Cl_2. To residue on filter paper add a little warm NH_4OH.

6. **Solution.** AgCl dissolves as $(AgCl)_2(NH_3)_3$. Add HNO_3 in excess. AgCl, white precipitate, or opalescence, indicates Ag.

7. **Residue.** A black compound, NH_2Hg_2Cl, indicates Hg_2.

Explanation of Table II.

1. **With HCl:**

$Pb(NO_3)_2 + 2HCl = PbCl_2 + 2HNO_3$;

$Hg_2(NO_3)_2 + 2HCl = Hg_2Cl_2 + 2HNO_3$;

$AgNO_3 + HCl = AgCl + HNO_3$.

Solution is taken *cold*, mainly on account of solubility of $PbCl_2$ in hot water. Even in the cold some $PbCl_2$ dissolves. Hence, Pb is found also in next Group.

Dilute HCl is used, since AgCl dissolves perceptibly in concentrated HCl.

A precipitate may form on adding HCl, even when no member of this Group is present. This is notably the case with Sb and Bi, which form basic chlorides, insoluble in water, but readily soluble *in excess* of HCl. S, SiO_2, and a few other substances are also precipitated under certain conditions. (See Fresenius, par. 182; Prescott, par. 547.)

Slight excess, as great excess interferes with precipitation of next Group.

The *filtrate is tested* to insure complete precipitation. This is recommended in general.

3. Washing removes HCl, which would interfere with the solution of $PbCl_2$ in hot water, and also remove traces of other Groups held by surface attraction, or, like Sb and Bi, precipitated with this Group. *Washings are added to the filtrate*, since they may contain parts of remaining Groups. Should addition of washings occasion turbidity in the acid filtrate, presence of Sb or Bi is indicated.

4. **Tests for Pb:**

1. $PbCl_2 + H_2SO_4 = \underline{PbSO_4} + 2HCl$. *Excess of* H_2SO_4, because $PbSO_4$ is less soluble in dilute H_2SO_4 than in water.
2. $PbCl_2 + H_2S = \underline{PbS} + 2HCl$. Very delicate. Black precipitate.
3. $PbCl_2 + K_2Cr_2O_7 + H_2O = \underline{PbCrO_4} + H_2CrO_4 + 2KCl$. Yellow precipitate, soluble in NaOH, reproduced by $HC_2H_3O_2$. (KI test also)

5. **With NH_4OH:**

$2AgCl + 3NH_4OH = (AgCl)_2(NH_3)_3 + 3H_2O$;

$Hg_2Cl_2 + 2NH_4OH = NH_2Hg_2Cl + NH_4Cl + 2H_2O$.

6. **With HNO_3:**

$(AgCl)_2(NH_3)_3 + 3HNO_3 = 2AgCl + 3NH_4NO_3$.

7. The Black Dimercurosammonium Chloride may be dried, mixed with Na_2CO_3, and the mixture heated in a bulb tube, when Hg will volatilize and condense in silvery globules. Or, it may be dissolved in aqua regia and the Cu test applied, as in Group IV, A, No. 6.

PROPERTIES OF GROUP IV., DIV. A.

MERCURY (Hg).—200.

Mercuric Combinations.

Soluble Compounds.—**Nitrate,** $Hg(NO_3)_2$; **Chloride,** $HgCl_2$; **Acetate,** $Hg(C_2H_3O_2)_2$; **Cyanide,** $Hg(CN)_2$; **Chlorate,** $Hg(ClO_3)_2$. The **Sulphate,** $HgSO_4$, is sparingly soluble. All, with the exception of the chloride, require acidulated water for permanent solution, as they are decomposed by water on standing, basic salts separating. $HgCl_2$, "corrosive sublimate," is made by dissolving Hg in aqua regia; $Hg(NO_3)_2$, by dissolving Hg in excess of HNO_3.

Insoluble Compounds.—**Oxide,** HgO, "red oxide of mercury," precipitated yellow from solutions of Hg salts by KOH and NaOH, added to supersaturation. Added short of saturation, these reagents give reddish basic salts. NH_4OH precipitates white basic salts; *e.g.*, from $HgCl_2$, NH_2HgCl. (See Prescott, par. 442, 443.)

There is no hydroxide.

Bromide, $HgBr_2$, white, sparingly soluble in water, precipitated from concentrated solutions by solutions of bromides; soluble in excess of reagent, in excess of Hg salt, and in HNO_3.

Iodide, HgI_2, salmon color, finally red, precipitated from solutions of Hg salts by solutions of iodides; soluble in excess of reagent, from formation of double salt $(KI)_2HgI_2$; soluble also in concentrated HCl and HNO_3.

Sulphide, HgS, black, precipitated by H_2S and $(NH_4)_2S$. At first the precipitate is white, owing to mixture with undecomposed original salt; it runs through different shades of color, and finally becomes black; insoluble in HCl and HNO_3, and in aqua regia. (See Explanation of Working Scheme.)

$SnCl_2$ reduces $HgCl_2$ to Hg_2Cl_2, white precipitate, which, on standing, darkens from deposit of Hg. (See Explanation of Working Scheme.)

Solutions of Hg compounds are easily reduced by Cu and other metals, the Hg being deposited as a silvery coating.

COPPER (Cu).—63.2.

A hard metal, reddish color, strong metallic luster. Sp. Gr. 8.95. It is malleable and ductile to a high degree, an excellent conductor of heat and electricity, and fuses with some difficulty. It is insoluble in HCl and cold H_2SO_4; soluble in HNO_3, in hot H_2SO_4, and in aqua regia. It is easily reduced from solutions of its salts by Fe and other metals, and by the electric current. It forms two series of salts: *cuprous*, in which the double atom, Cu_2, is bivalent; and *cupric*, in which the single atom, Cu, is bivalent. The cuprous salts are insoluble in water, and as a rule are not stable.

Soluble Compounds.—**Cupric Nitrate,** $Cu(NO_3)_2$; **Sulphate,** $CuSO_4$; **Acetate,** $Cu(C_2H_3O_2)_2$; **Chloride,** $CuCl_2$; **Bromide,** $CuBr_2$; **Chlorate,** $Cu(ClO_3)_2$. Crystallized and in solution, they

all have a blue or green color; anhydrous cupric salts are white.

Insoluble Compounds.—Oxides: cuprous, Cu_2O; cupric, CuO. Cu_2O is a carmine-red powder, changed to CuO by heating in air or in oxygen; soluble in acids and in NH_4OH. CuO is brownish-black; soluble in acids; easily reduced to metallic Cu by hydrogen or carbon.

Hydroxides: cuprous, $Cu_2(OH)_2$; cupric, $Cu(OH)_2$. Cupric, deep blue, is precipitated by KOH and NaOH; readily soluble in acids. Boiling the precipitate in its menstruum causes it to blacken, from formation of CuO; on standing, $Cu(OH)_2$ changes to a black basic compound. In presence of certain organic substances, notably tartaric acid and its salts, the precipitate either does not form or redissolves. From this alkaline Cu solution, grape sugar throws down orange to red $Cu_2(OH)_2$ (Fehling's test for sugar).

NH_4OH gives pale blue basic salts, dissolving to a deep blue liquid. (See Working Scheme and Explanation.)

Sulphide, CuS, brownish black, precipitated by H_2S and $(NH_4)_2S$; somewhat soluble in $(NH_4)_2S_x$, yellow ammonium sulphide; readily soluble in HNO_3; scarcely soluble in HCl; insoluble in H_2SO_4; soluble in solution of KCN.

The **Carbonate, Phosphate,** and double **Cyanides** are also insoluble; the **Iodide,** sparingly soluble.

For reactions with $K_4Fe(CN)_6$, see Explanation of Working Scheme.

For reactions with acids of As, see Acid Analysis, Gr. I.

BISMUTH (Bi).—208.

A hard, brittle substance, strong metallic luster, white with reddish tinge. This last characteristic serves to distinguish it from Sb, which it closely resembles in other respects. Sp. Gr. 9.75. It melts at a rather low temperature, which is still further lowered by alloying with other metals; hence its use in making "fusible metals." It is insoluble in HCl; attacked by concentrated H_2SO_4; readily soluble in HNO_3.

Soluble Compounds. — Nitrate, $Bi(NO_3)_3$; **Chloride,** $BiCl_3$; **Sulphate,** $Bi_2(SO_4)_3$, are soluble in water acidulated with the corresponding acid, but are decomposed by pure water, with precipitation of basic salts; *e.g.*, from $BiCl_3$, BiOCl; from $Bi(NO_3)_3$, $BiONO_3$.

Insoluble Compounds.—Oxides, four in number. Of these none are of analytical importance.

Hydroxide, $Bi(OH)_3$, white, precipitated by KOH, NaOH, and NH_4OH; soluble in HCl. (See Working Scheme.)

Sulphide, Bi_2S_3, black, precipitated by H_2S and $(NH_4)_2S$; insoluble in dilute acids; soluble in moderately concentrated HNO_3.

CADMIUM (Cd).—112.

A lustrous white metal, rather soft, very malleable and ductile. Sp. Gr. 8.66. It is soluble in HCl, H_2SO_4, HNO_3.

Soluble Compounds.—Nitrate, $Cd(NO_3)_2$; **Chloride,** $CdCl_2$; **Sulphate,** $CdSO_4$.

Insoluble Compounds.—Oxide, CdO, brown powder, soluble in HCl, H_2SO_4, HNO_3.

Hydroxide, $Cd(OH)_2$, white, precipitated by KOH and NaOH; soluble in HCl, H_2SO_4, and HNO_3. NH_4OH gives the same precipitate, but excess redissolves it.

Sulphide, CdS, bright yellow, precipitated by H_2S and $(NH_4)_2S$; insoluble in cold dilute acids; soluble in boiling dilute acids; insoluble in KCN.

TABLE III.—ANALYSIS OF GROUP IV., DIV. A.

Hg, Pb, Bi, Cu, Cd.

1. Heat to boiling the filtrate from Group V, or the solution found not to contain Group V, acidulated with **HCl**; add **H_2S**, and filter.

2. **Filtrate.** Groups III, II, I. Reserve to test for these.

3. **Precipitate.** HgS, PbS, Bi_2S_3, CuS, CdS. As_2S_3, As_2S_5, Sb_2S_3, SnS, SnS_2. Wash with hot water until washings have no acid reaction. Transfer to an evaporating dish, digest with $(NH_4)_2S_x$ (the yellow Sulphide), heat gently, and filter.

4. **Solution.** Group IV, Div. B. Reserve to test by next table.

5. **Residue.** HgS, PbS, Bi_2S_3, CuS, CdS. Wash, transfer to an evaporating dish, add dilute **HNO_3**, heat, and filter.

6. **Residue.** HgS. Dissolve in **aqua regia**, dilute with water, and place in the solution a bit of clean **Cu**. Silvery coating, Hg.

7. **Solution.** $Pb(NO_3)_2$, $Bi(NO_3)_3$, $Cu(NO_3)_2$, $Cd(NO_3)_2$. To a small portion add **H_2SO_4** (dilute) in excess and let stand. Should a precipitate form, add to rest dilute **H_2SO_4**, let stand, and filter.

8. **Precipitate.** White, $PbSO_4$, indicates Pb.

9. **Filtrate.** $Bi(NO_3)_3$, $Cu(NO_3)_2$, $Cd(NO_3)_2$. Add **NH_4OH** in excess, and filter.

10. **Precipitate.** White ppt., $Bi(OH)_3$, indicates Bi. Confirm by dissolving in a few drops conc. **HCl** + a crystal of **$KClO_3$**, and adding to a beaker of clear water. White cloud, BiOCl.

Blue coloration indicates Cu. Confirm by boiling down, and adding **$HC_2H_3O_2$** and **$K_4Fe(CN)_6$**. Reddish-brown ppt., $Cu_2Fe(CN)_6$, indicates Cu.

11. **Filtrate.** $(NH_3)_2$-CuO . $(NH_4NO_3)_2$, $Cd(OH)_2$. Add sol. **KCN** until blue color disappears, then **H_2S**. Yellow ppt., CdS, indicates Cd.

Explanation of Table III.

1. **With H_2S:**

$Hg(NO_3)_2 + H_2S = HgS + 2HNO_3$; same for Cu and Cd.

$2Bi(NO_3)_3 + 3H_2S = Bi_2S_3 + 6HNO_3$.

$2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$.

$2H_3AsO_4 + 5H_2S = As_2S_5 + 8H_2O$.

$2H_3AsO_4 + 5H_2S = As_2S_3 + 8H_2O + 2S$.

(See *American Journal of Chemistry*, November, 1888, p. 459. Prescott, note ad calc. p. 124.)

$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl$.

$SnCl_2 + H_2S = SnS + 2HCl$.

$SnCl_4 + 2H_2S = SnS_2 + 4HCl$.

The solution is first *acidulated* in order to insure precipitation of the sulphides of As and some others, which form only in presence of free acid. In continued analysis this acidulation is unnecessary, since sufficient HCl comes through from Group V. Excess of acid interferes with precipitation of the sulphides of Sb and Sn. Hence, when these metals are suspected, allow H_2S to run into the acidified solution long enough to precipitate As_2S_3, then add hot water and continue to pass H_2S.

Should the precipitate be of a light color, yellow or orange, it will be found to consist of Sb_2S_3, SnS_2, As_2S_3, or CdS. A white precipitate is merely separated S, indicating Fe_2 compounds, which are reduced to Fe state by H_2S:

$Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S$.

From solutions of H_3AsO_4 and arsenates, the sulphides come down only after long standing.

Heating promotes precipitation and filtering.

3. Before applying $(NH_4)_2S_x$, the precipitate must be *washed clear of all acid*, as acids decompose the solvent, depositing S.

$(NH_4)_2S_x$, the *yellow sulphide*, may be prepared by adding to the colorless reagent a pinch of S, and heating.

Heat *gently*, as great heat ruins composition of solvent. Use smallest possible quantity.

Reactions:

$As_2S_3 + 2(NH_4)_2S_x = (NH_4)_4As_2S_5 + 2(x - 1)S$.

$As_2S_5 + 3(NH_4)_2S_x = 2(NH_4)_3AsS_4 + 3(x - 1)S$.

$Sb_2S_3 + 3(NH_4)_2S_x = 2(NH_4)_3SbS_4 + (3x - 5)S$.

$SnS + (NH_4)_2S_x = (NH_4)_2SnS_3 + (x - 2)S$.

$SnS_2 + (NH_4)_2S_x = (NH_4)_2SnS_3 + (x - 1)S$.

(See *Watts's Dictionary of Chemistry*, second edition, Vol. I., p. 316, and under *Thiosalts of Arsenic;* Prescott, par. 457, 477.)

5. $3PbS + 8HNO_3 = 3Pb(NO_3)_2 + 3S + 2NO + 4H_2O$; same for Cu and Cd.

$Bi_2S_3 + 8HNO_3 = 2Bi(NO_3)_3 + 3S + 2NO + 4H_2O$.

Wash to remove $(NH_4)_2S_x$.

Dilute HNO_3, as concentrated acid oxidizes PbS, leaving $PbSO_4$, insoluble, with HgS:

$3PbS + 8HNO_3$ (conc.) $= 3PbSO_4 + 8NO + 4H_2O$.

(See Prescott, par. 564.)

6. **Reaction with Aqua Regia:**

$$HgS + 2Cl = HgCl_2 + S.$$

Reaction with Cu:

$$HgCl_2 + Cu = Hg + CuCl_2.$$

Coating becomes bright on rubbing.

7. **Reaction with H_2SO_4:**

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3.$$

The test for Pb is first made with a *small portion* of the solution to guard against a large excess of free acid, which would require a quantity of NH_4OH to neutralize it, thus diluting solution.

9. The first portions of NH_4OH produce a precipitate of $Cu(OH)_2$:

$$Cu(NO_3)_2 + 2NH_4OH = Cu(OH)_2 + 2NH_4NO_3.$$

$Cu(OH)_2$ readily dissolves *in excess* of reagent, with formation of cuprodiammonium nitrate giving an intensely blue coloration:

$$Cu(NO_3)_2 + 4NH_4OH = (NH_3)_2CuO.(NH_4NO_3)_2 + 3H_2O.$$

(See Fresenius, par. 120, 8; Prescott, par. 340.)

Since CuS dissolves somewhat in the $(NH_4)_2S_x$ used to separate the two divisions of the Group, the amount of Cu salt here may be too small to give the reaction with NH_4OH. Hence the ferrocyanide test is applied, the red precipitate being more noticeable than a faint blue coloration:

$$2Cu(NO_3)_2 + K_4Fe(CN)_6 = Cu_2Fe(CN)_6 + 4KNO_3.$$

$Cd(OH)_2$ also dissolves in excess of NH_4OH:

$$Cd(NO_3)_2 + 2NH_4OH = Cd(OH)_2 + 2NH_4NO_3.$$

$Bi(OH)_3$ is insoluble:

$$Bi(NO_3)_3 + 3NH_4OH = Bi\,(OH)_3 + 3NH_4NO_3.$$

10. The confirmatory test consists in the decomposition of $BiCl_3$ by large excess of water, with formation of the oxychloride, which appears as a beautiful white cloud:

$$Bi(OH)_3 + 3HCl = BiCl_3 + 3H_2O;$$

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

BiOCl dissolves readily in HCl, hence the caution about using small quantity of solvent.

11. KCN prevents formation of CuS, black, which would overwhelm the yellow CdS. On adding H_2S to solution of $Cd(OH)_2$:

$$Cd(OH)_2 + H_2S = CdS + 2H_2O.$$

(See Prescott, par. 375.)

PROPERTIES OF GROUP IV., DIV. B.

ARSENIC (As).—75.

A steel-gray, lustrous substance, very brittle. Sp. Gr. 5.72. It combines readily with many of the elements. Heated in air, it takes fire at a high temperature, burning with a bluish flame, and giving off fumes of As_2O_3. It is scarcely attacked by HCl, but is oxidized to arsenic acid by H_2SO_4, HNO_3, and aqua regia. In physical properties, As resembles the metals, but the acid-forming nature of its oxides determines its non-metallic character. It is here classed among the bases, owing to the fact that H_2S decomposes solutions of both arsenious and arsenic compounds, precipitating As among bases of Group IV. The special tests for the acids of arsenic will be found in Acid Analysis, Gr. I, A.

Arsenious Oxide, As_2O_3, white ("white arsenic"), is either a colorless, transparent vitreous, or white "porcelain-like," body, yielding a heavy white powder. It is easily reduced to elemental As by carbon. As_2O_3 is very sparingly soluble in cold water, less sparingly in hot water, easily in HCl. The water solution is supposed to contain H_3AsO_3, arsenious acid, but this compound has never been separated. Its salts, however, the *arsenites*, are known. Of these, those with alkali metals are the only ones soluble in water. The more important reactions of the arsenites are given in Acid Analysis, Gr. I, A, 2.

Arsenious Sulphide, As_2S_3, lemon-yellow, precipitated by H_2S, readily from acidulated solutions of arsenites, very tardily from solutions of arsenates; soluble in $(NH_4)_2S_x$ and in $(NH_4)_2CO_3$. (See Working Scheme and Explanation.)

Arsenic Oxide, As_2O_5, white, dissolves in water, giving arsenic acid, H_3AsO_4. The latter is a translucent, crystalline body, very poisonous; soluble in HCl, somewhat soluble in water. Heated, it yields metarsenic acid, $HAsO_3$, and pyro-arsenic acid, $H_4As_2O_7$. Of the normal arsenates (salts of H_3AsO_4), those of Group I metals alone are soluble in water. All dissolve in strong mineral acids. (See Acid Analysis, Gr. I, A, 3, for reactions of arsenic acid and arsenates.)

Marsh's Test for Arsenic.—If a solution containing any compound of As is brought in contact with Zn and dilute H_2SO_4, in a hydrogen generator, the nascent H and the As compound react to form AsH_3 (arsenic hydride, arsine, arseniuretted hydrogen), a colorless, very poisonous gas. When lighted, AsH_3 burns with a bluish flame, the products of combustion being As_2O_3 and H_2O. If a cold object, usually a piece of porcelain (on account of its whiteness), is held before the flame, the temperature of the gas is lowered and

oxidation partially prevented. As is deposited in lustrous, steel-gray spots. The As deposit is soluble in solution of sodium hypochlorite. This property of the deposit, and its luster, distinguish As from Sb, which under the same circumstances gives a velvety-brown, smoky deposit, insoluble in the hypochlorite solution. Passed into $AgNO_3$ solution, AsH_3 precipitates Ag, the As passing into solution as H_3AsO_3. (For details, see Fresenius, par. 132, *sq.*; Prescott, par. 464, *sq.*; Roscoe and Schorlemmer, p. 534.)

ANTIMONY (Sb).—120.

A bluish-white, lustrous substance, hard, very brittle, easily fusible. Sp. Gr. 6.7. Heated on charcoal, it burns to the white Sb_2O_3, giving dense fumes, part of which are deposited on the charcoal as a white incrustation. A peculiar characteristic of Sb is that it continues to glow after the flame has been removed, the assay becoming covered with a network of acicular crystals of Sb_2O_3. Sb is slowly soluble in concentrated H_2SO_4, and in $H_2C_4H_4O_6$; soluble, when in form of powder, in HCl (concentrated); easily soluble in aqua regia. It is not dissolved by HNO_3, but is converted into an oxide, either Sb_2O_3 or Sb_2O_5, according to the degree of concentration of the acid. It forms both acids and bases.

Soluble Compounds.—**Antimonious Chloride,** $SbCl_3$, is soluble in water acidulated with HCl, but is decomposed by pure water, with precipitation of an oxychloride. The **Tartrate,** and the **Potassio Antimonyl Tartrate,** $KSbOC_4H_4O_6$, "tartar emetic," are also soluble.

Insoluble Compounds.—The chief reactions will be found in Explanation of Working Scheme.

Sulphide, Sb_2S_3, orange-red, precipitated by H_2S from solutions not too strongly acid; soluble in $(NH_4)_2S_x$ and in HCl; insoluble in $(NH_4)_2CO_3$.

With nascent H, solutions containing Sb form SbH_3, which, passed into $AgNO_3$ solution, precipitates Ag_3Sb, black. The flame of SbH_3 leaves a smoky deposit on porcelain. If the hydrogen generator contain Pt in contact with the Zn, some of the Sb solution is reduced, and the Sb deposited as a black stain on the Pt, soluble in $H_2C_4H_4O_6$. (See Working Scheme and Explanation.)

TIN (Sn).—118.

A lustrous white metal, soft and malleable, melting at 228°. Sp. Gr. 7.29. It is soluble in HCl, aqua regia, and H_2SO_4. HNO_3 fails to dissolve it, unless very dilute, but converts it into metastannic acid, $H_{10}Sn_5O_{15}$, an insoluble white powder.

There are two classes of compounds of Sn: *stannous*, in which Sn is bivalent, and *stannic*, in which Sn is quadrivalent.

Soluble Compounds. — **Stannous Chloride,** $SnCl_2$, formed by dissolving the metal in HCl, requires water strongly acidulated with HCl. The other haloids dissolve in pure water, but are decomposed by great excess.

Stannous Sulphate, $SnSO_4$, formed by treating the metal with H_2SO_4, dissolves in pure water.

Stannous Nitrate, $Sn(NO_3)_2$, formed by treating the metal with very dilute HNO_3, requires acidulated water.

Stannous Acetate, $Sn(C_2H_3O_2)_2$, is soluble in water.

Stannic Chloride, $SnCl_4$, formed by dissolving the metal in aqua regia, is decomposed by excess of pure water. **Bromide,** $SnBr_4$, and **Iodide,** SnI_4, also require acidulated water.

The remaining soluble forms are **Sulphate,** $Sn(SO_4)_2$; **Acetate,** $Sn(C_2H_3O_2)_4$; **Oxalate,** $Sn(C_2O_4)_2$.

Insoluble Compounds.—Stannous Oxide, SnO, grayish-black, soluble in HCl, converted by HNO_3 to metastannic acid.

Stannic Oxide, SnO_2, white to yellow, is both acid- and base-forming. Its acids are stannic, H_2SnO_3, and metastannic, $H_{10}Sn_5O_{15}$.

Stannous Hydroxide, $Sn(OH)_2$, white, precipitated from solution of stannous salts by alkaline hydroxides and carbonates. The precipitate is soluble in excess of KOH and NaOH, insoluble in excess of the other precipitants.

From solutions of stannic salts the same reagents give **Stannic Acid,** H_2SnO_3, white, soluble in excess of KOH and NaOH, soluble also in acids.

Stannous Sulphide, SnS, dark brown, precipitated from solutions of stannous salts by H_2S and soluble sulphides. The precipitate is soluble in $(NH_4)_2S_x$, the yellow sulphide; reprecipitated by acids as SnS.

Stannic Sulphide, SnS_2, yellow, precipitated from solutions of stannic salts by H_2S and soluble sulphides; soluble in $(NH_4)_2S_x$. (See Working Scheme and Explanation.)

Zn reduces Sn from its solutions as a grayish, spongy mass, soluble in HCl as $SnCl_2$. This solution reduces $HgCl_2$ to Hg_2Cl_2 and finally, in part, to Hg. (Working Scheme and Explanation.)

Explanation of Table IV.

1. The sulphides are reproduced from the ammonium thiosalts, by decomposition with HCl:

$$(NH_4)_4As_2S_5 + 4HCl = As_2S_3 + 4NH_4Cl + 2H_2S.$$
$$2(NH_4)_3AsS_4 + 6HCl = As_2S_5 + 6NH_4Cl + 3H_2S.$$
$$2(NH_4)_3SbS_4 + 6HCl = Sb_2S_5 + 6NH_4Cl + 3H_2S.$$
$$(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S.$$
$$(NH_4)_2S_x + 2HCl = 2NH_4Cl + H_2S + (x-1)S.$$

Observe that both arsenious and arsenic sulphides are reproduced, while from Sb only antimonic sulphide is formed, and from Sn only stannic, no matter in what state of oxidation the bases were originally present. Also, that S is always precipitated, so that the mere formation of a precipitate proves nothing.

3. As is removed by solution of its sulphides in $(NH_4)_2CO_3$:

$$As_2S_3 + 3(NH_4)_2CO_3 = (NH_4)_3AsO_3 + (NH_4)_3AsS_3 + 3CO_2.$$
$$As_2S_5 + 3(NH_4)_2CO_3 = (NH_4)_3AsO_3 + (NH_4)_3AsS_3 + 3CO_2 + 2S.$$

HCl is first entirely removed by *washing*, else the $(NH_4)_2CO_3$ would be lost in neutralizing it. $(NH_4)_2CO_3$ free from NH_4OH is preferable to the ordinary reagent, since NH_4OH dissolves somewhat SnS_2 and Sb_2S_5. Some As may remain behind, but may be detected in No. 6.

4. **With HCl:**

$$(NH_4)_3AsO_3 + (NH_4)_3AsS_3 + 6HCl = As_2S_3 + 6NH_4Cl + 3H_2O.$$

The acid must be added *slowly*, to allow CO_2, from undecomposed $(NH_4)_2CO_3$, to escape without loss of solution. The test is best made in a beaker.

$As_2S_3 + 6NH_4OH = (NH_4)_3AsO_3 + (NH_4)_3AsS_3 + 3H_2O$

TABLE IV.—ANALYSIS OF GROUP IV., DIV. B.

As, Sn, Sb.

1. To solution No. 4, Group V, Div. A—containing $(NH_4)_4As_2S_5$, $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$, $(NH_4)_2SnS_3$—add dil. **HCl**, and filter.

2. Filtrate. —NH_4Cl. Reject.

3. Precipitate. As_2S_3, As_2S_5, Sb_2S_5, SnS_2. Wash, to remove all HCl, transfer to evaporating dish, treat with cold $(NH_4)_2CO_3$, and filter.

4. Solution. $(NH_4)_3AsO_3 + (NH_4)_3AsS_3$. Add dil. **HCl**; yellow precipitate, As_2S_3.

Confirmatory test: Dry, mix with equal parts Na_2CO_3 and **KCN**, and heat in dry bulb tube. As sublimes and is deposited as a black mirror.

5. Precipitate. Sb_2S_5, SnS_2. Dissolve in conc. **HCl** + crystal $KClO_3$. Add sol. to generator containing dil. **HCl** with **Zn** and **Pt** foil in contact. Receive gas in sol. $AgNO_3$ (10 drops reagent to ½ test tube of water). Allow to run some time.

6. In test tube. Black ppt., Ag_3Sb, indicates Sb. Sol. may contain As. Test as follows: filter off ppt., and to filtrate add dil. **HCl**, to remove free $AgNO_3$. Filter, and to filtrate add H_2S. Yellow ppt., As_2S_3, indicates As. Confirm as in 4.

7. In generator. Black coating or stain on **Pt** is Sb; grayish, spongy deposit on **Zn** is Sn. Wash coated **Zn** and remove. Remove Sn from Zn by rinsing, place in an evaporating dish, and heat with moderately dil. **HCl**. Sn dissolves as $SnCl_2$. To sol. add $HgCl_2$. White ppt., Hg_2Cl_2, indicates Sn. Sb remains on foil. Place in sol. $H_2C_4H_4O_6$ + few drops dil. HNO_3. To sol. add H_2S. Orange ppt., Sb_2S_3, indicates Sb.

If traces of Sb_2S_5 or SnS_2 have dissolved in the $(NH_4)_2CO_3$, a yellowish precipitate may form here, even in the absence of As. Hence the need of its confirmatory test, for the success of which materials must be perfectly dry. Should water make its appearance, it must be wiped away. (See Fresenius, par. 132, 13.)

Reaction for confirmatory test:

$$As_2S_3 + 3Na_2CO_3 + 3KCN = 2As + 3Na_2S + 3KCNO + 3CO_2.$$

5. **With HCl and $KClO_3$:**

$$Sb_2S_5 + 6Cl = 2SbCl_3 + 5S.$$
$$Sb_2S_5 + 10Cl + 5H_2O = Sb_2O_5 + 10HCl + 5S.$$
$$SnS_2 + 4Cl = SnCl_4 + 2S.$$

When introduced into the generator, with Zn and Pt, the Sb solution is partly electrolyzed, and the metal deposited on the *negative* (Pt) *plate*, while some SbH_3 is formed; Sn is entirely reduced on the Zn as a *spongy mass, not adhering closely:*

$$Sb_2O_5 + 8Zn + 16HCl = 2SbH_3 + 8ZnCl_2 + 5H_2O.$$
$$Sb_2O_5 + 5Zn + 10HCl = 2Sb + 5H_2O + 5ZnCl_2.$$
$$SbCl_3 + 3Zn + 3HCl = SbH_3 + 3ZnCl_2.$$
$$2SbCl_3 + 3Zn = 2Sb + 3ZnCl_2.$$
$$SnCl_4 + 2Zn = Sn + 2ZnCl_2.$$

6. The SbH_3 in $AgNO_3$ solution throws down Ag_3Sb:

$$SbH_3 + 3AgNO_3 = Ag_3Sb + 3HNO_3.$$

If As has not been entirely removed by $(NH_4)_2CO_3$, AsH_3 will be formed in the generator, and cause a black precipitate in the $AgNO_3$ solution, easily mistaken for Ag_3Sb, but consisting only of metallic Ag, all the As passing into solution as H_3AsO_3:

$$AsH_3 + 6AgNO_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3.$$

To test for As, the black precipitate is filtered off, free $AgNO_3$ in the filtrate is precipitated by HCl, in order to prevent the formation of black Ag_2S, and the filtrate is tested with H_2S.

7. All of the Sn and some of the Sb remain in the elemental state on the metals in the generator. The Zn must not be allowed to dissolve entirely, else the Sn will be attacked by the HCl present. Sn is rinsed away from the Zn, transferred to an evaporating dish and boiled with moderately concentrated HCl. Sn dissolves as $SnCl_2$, and is tested for with $HgCl_2$:

$$Sn + 2HCl = SnCl_2 + 2H.$$
$$SnCl_2 + 2HgCl_2 = Hg_2Cl_2 + SnCl_4.$$

On standing: $Hg_2Cl_2 + SnCl_2 = Hg + SnCl_4$.

Sb remains undissolved on Pt, which is next placed in a solution of $H_2C_4H_4O_6$ + a few drops dilute HNO_3:

$$2Sb + H_2C_4H_4O_6 + 2H_2O = (SbO)_2C_4H_4O_6 + 6H.$$
$$2Sb + 2HNO_3 = Sb_2O_3 + H_2O + 2NO.$$
$$Sb_2O_3 + H_2C_4H_4O_6 = (SbO)_2C_4H_4O_6 + H_2O.$$

With H_2S:

$$(SbO)_2C_4H_4O_6 + 3H_2S = Sb_2S_3 + H_2C_4H_4O_6 + 2H_2O.$$

PROPERTIES OF GROUP III.

COBALT (Co).—58.8.

A steel-gray, lustrous metal; nearly white when polished; hard, rather malleable, very ductile; feebly magnetic, retaining magnetism even at red heat. Sp. Gr. 8.5. It does not oxidize in air; decomposes steam at red heat. It is soluble in mineral acids, giving *cobaltous* salts, in which Co is bivalent. *Cobaltic* salts (Co_2 hexivalent) are little known.

Soluble Compounds.—**Cobaltous Nitrate,** $Co(NO_3)_2$; **Chloride,** $CoCl_2$, and other haloids; **Sulphate,** $CoSO_4$; **Acetate,** $Co(C_2H_3O_2)_2$; **Chlorate,** $Co(ClO_3)_2$. Cobaltous salts are as a rule red in crystals, lilac or blue when anhydrous. Their solutions are blue when concentrated, pink when dilute.

Insoluble Compounds.—**Cobaltous Oxide,** CoO, is a greenish-brown powder, soluble in acids, giving cobaltous salts. It imparts a blue color to the borax bead or to glass.

Cobaltic Oxide, Co_2O_3, is a steel-gray, lustrous solid, soluble in concentrated acids, giving mostly cobaltous salts.

Cobalto-Cobaltic Oxide, Co_3O_4, is a black, amorphous powder, slowly soluble in concentrated H_2SO_4.

Cobaltous Hydroxide, $Co(OH)_2$, rose-red, is precipitated by alkalies from solutions of cobaltous salts. The precipitate at first consists of blue basic salts, slowly changing on heating to $Co(OH)_2$. If exposed to air, the blue basic salts absorb O, and turn green, forming a *cobalto-cobaltic* hydroxide. $Co(OH)_2$ is soluble in excess of NH_4OH, and its formation altogether prevented by presence of NH_4Cl. It is also soluble in acids.

Cobaltic Hydroxide, $Co_2(OH)_6$, black, is formed when $Co(OH)_2$ is treated with Cl or Br, in presence of NaOH.

There are several cobalto-cobaltic hydroxides.

Cobaltous Sulphide, CoS, black, is precipitated only imperfectly by H_2S, not at all in presence of free acid, but is completely precipitated by $(NH_4)_2S$. It is soluble in aqua regia and HNO_3; insoluble in dilute HCl, slightly soluble in concentrated HCl. Precipitation is promoted by presence of NH_4Cl. In the air, CoS oxidizes to soluble $CoSO_4$.

Cyanide, $Co(CN)_2$, brownish-white; precipitated by KCN; soluble in excess of precipitant as a double cyanide of Co and K. (See Working Scheme and Explanation.) There are various complex cyanides.

Alkaline carbonates precipitate **Basic Cobaltous Carbonate,** peach-red, turning violet on boiling from separation of CO_2. It is soluble in $(NH_4)_2CO_3$.

KNO_2, in strong solution, together with $HC_2H_3O_2$, gives, on standing in a warm place, yellow crystals of **Potassium Cobaltic Nitrite,** $(KNO_2)_6.Co_2(NO_2)_6$.

NICKEL (Ni).—58.6.

A white metal, with slight grayish-yellow tinge; very lustrous; capable of a high polish; hard, very tenacious, malleable, and ductile. It may be magnetized, but loses its magnetism at red heat; fuses with difficulty. Sp. Gr. 8.97 to 9.26. Ni does not oxidize in air; hence it is used extensively as a coating on iron, to prevent rusting. It is used in coinage alloyed with Cu or with Cu and Zn. The latter alloy is German silver. Ni is soluble in HCl and dilute H_2SO_4, with evolution of H, and in concentrated H_2SO_4, with evolution of SO_2; soluble also in dilute HNO_3, but passive in concentrated HNO_3. In all these cases *nickelous* salts, Ni bivalent, are formed. *Nickelic* compounds, Ni_2 sexivalent, are obtained by oxidation of nickelous compounds.

Soluble Compounds.—**Nickelous Nitrate,** $Ni(NO_3)_2$; **Chloride,** $NiCl_2$, and other haloids; **Sulphate,** $NiSO_4$; **Acetate,** $Ni(C_2H_3O_2)_2$; **Chlorate,** $Ni(ClO_3)_2$. Nickelous salts are green in crystals or in solution, yellow when anhydrous.

Insoluble Compounds.—**Nickelous Oxide,** NiO, a green powder, yellow when heated; soluble in acids, giving nickelous salts.

Nickelic Oxide, Ni_2O_3, black powder; soluble in acids, giving nickelous salts.

Nickelo-Nickelic Oxide, Ni_3O_4, a gray solid, corresponds to Co_3O_4.

Nickelous Hydroxide, $Ni(OH)_2$, pale green, precipitated by alkaline hydroxides from solutions of nickelous salts. The precipitate is soluble in excess of NH_4OH; its formation is prevented by presence of NH_4Cl.

Nickelic Hydroxide, $Ni_2(OH)_6$, black, formed by Cl or Br and NaOH in nickelous solutions. (See Working Scheme and Explanation.)

Nickelous Sulphide, NiS, brownish-black, is precipitated only imperfectly by H_2S; not at all in presence of free acid; completely precipitated by $(NH_4)_2S$. It is slightly soluble in excess of $(NH_4)_2S$; insoluble in dilute HCl; soluble in aqua regia. It oxidizes in air to soluble $NiSO_4$.

Nickelous Cyanide, $Ni(CN)_2$, yellowish-green, precipitated by KCN; soluble in excess of precipitant as $(KCN)_2.Ni(CN)_2$. (See Explanation of Working Scheme.)

Alkaline carbonates give **Basic Nickelous Carbonate,** green, soluble in excess of $(NH_4)_2CO_3$.

MANGANESE (Mn).—55.

A gray-white, dull metal, very hard and brittle. Sp. Gr. 7.14 to 7.20. It oxidizes in moist air and in water; hence it must be kept under naphtha. It is soluble in acids, giving manganous salts. Alloys with Fe are used in Bessemer steel process (Spiegeleisen, ferromanganese). Mn is both base- and acid-forming. In *manganous* salts, Mn is bivalent; in *manganic* salts, Mn_2 is sexivalent.

Soluble Compounds.—**Manganous Nitrate,** $Mn(NO_3)_2$; **Chloride,** $MnCl_2$, and other haloids; **Sulphate,** $MnSO_4$; **Acetate,** $Mn(C_2H_3O_2)_2$. Manganous salts are mostly pink.

Insoluble Compounds.—**Manganous Oxide,** MnO, a grass-green powder. Heated in air, it is converted into Mn_2O_3 and Mn_3O_4. It is soluble in acids, giving manganous salts.

Manganic Oxide, Mn_2O_3, a black powder. Its salts are rare.

Mangano-Manganic Oxide, Mn_3O_4, reddish-brown, giving manganous salts with acids.

Manganese Peroxide, MnO_2, black (dioxide, black oxide), the well-known oxidizing agent, used in the preparation of oxygen, the halogens, etc.; soluble in acids, giving manganous salts. MnO_2 gives rise to the *manganates* K_2MnO_4, and *permanganates* $K_2Mn_2O_8$. The latter are important oxidizing agents. They are all soluble in water.

Manganous Hydroxide, $Mn(OH)_2$, white, precipitated by alkaline hydroxides; soluble in NH_4Cl and other salts of NH_4, and in NH_4OH on account of NH_4 salt formed. It turns brown in the air, by oxidation to $Mn_2O_2(OH)_2$.

Manganous Sulphide, MnS, flesh color, buff, precipitated by $(NH_4)_2S$; soluble in all dilute acids, including $HC_2H_3O_2$ (distinction from ZnS); not precipitated by H_2S, owing to the formation of an acid in the reaction. It turns brown to black in air, by oxidation.

Carbonates give $MnCO_3$, white, oxidizing in air to $Mn_2O_3(OH)_2$, brown.

Fusion with alkalies and oxidizing agents converts manganese compounds into manganates, "peacock green."

ZINC (Zn).—65.

A bluish-white metal, very lustrous, moderately hard. Sp. Gr. 7.14. It is brittle at ordinary temperatures, malleable at 100° to 150°, brittle again above 200°; melts at 443°, and boils at 1040°, burning with a bluish-white flame to ZnO. Pure Zn dissolves slowly, commercial Zn rapidly, in acids and alkalies. With HCl, H_2SO_4, and $HC_2H_3O_2$, H is given off; with dilute HNO_3, no gas is given off, NH_4NO_3 being formed; with concentrated HNO_3, NO is given off. The solution in alkalies contains zincates; *e.g.*, K_2ZnO_2. Some alloys of Zn are of great importance. Brass consists of Zn and Cu; German silver, of Zn with Cu and Ni; galvanized iron is Fe coated with Zn.

Soluble Compounds.—Nitrate, $Zn(NO_3)_2$; **Chloride,** $ZnCl_2$, and other haloids; **Sulphate,** $ZnSO_4$; **Chlorate,** $Zn(ClO_3)_2$; **Acetate,** $Zn(C_2H_3O_2)_2$. All are deliquescent, except $ZnSO_4$, which effloresces.

Insoluble Compounds.—Oxide, ZnO, "flowers of zinc," white, formed by igniting Zn and many of its compounds in air. It is yellow when hot. It is soluble in acids.

Hydroxide, $Zn(OH)_2$, white, precipitated by alkaline hydroxides; soluble in excess as zincate; soluble also in acids.

Sulphide, ZnS, the only white sulphide, precipitated completely by $(NH_4)_2S$; completely by H_2S in presence of $HC_2H_3O_2$; partially from neutral solutions; not at all from mineral acid solutions; soluble in dilute HCl.

Carbonates give **Basic Carbonate,** white, soluble in excess of $(NH_4)_2CO_3$.

IRON (Fe).—56.

Pure iron is a very rare metal. It is prepared by electrolysis, or by reduction of its compounds by carbon or hydrogen. It is a lustrous, grayish-white substance, softer and more malleable than ordinary wrought iron, but less tenacious; fuses only at a very high temperature. Pure iron may be magnetized, but will not retain its magnetism. Finely divided, it will burn in ordinary air. All the ordinary varieties of iron contain carbon, and usually silicon and other substances. Cast iron contains from 1.5% to 4.75% of carbon; wrought iron, less than .6%; steel is, as a rule, intermediate, although certain varieties of mild steel may contain less carbon than wrought iron. As the percentage of

carbon increases, the fusibility increases, but the malleability decreases, cast iron, the most easily fusible variety, being brittle. (For description of the metallurgy of iron, and account of properties of the different varieties, see Dictionary of Applied Chemistry, Thorpe, Vol. II.)

Iron dissolves in HCl, in dilute H_2SO_4, and cold dilute HNO_3, giving *ferrous* salts (Fe bivalent), and in hot concentrated H_2SO_4, and hot, moderately dilute HNO_3, giving *ferric* salts, (Fe_2 sexivalent). In concentrated HNO_3 it becomes "passive."

Soluble Compounds. — **Ferrous Nitrate,** $Fe(NO_3)_2$; **Chloride,** $FeCl_2$, and other haloids; **Sulphate,** $FeSO_4$; **Acetate,** $Fe(C_2H_3O_2)_2$; **Chlorate,** $Fe(ClO_3)_2$.

Ferric Nitrate, $Fe_2(NO_3)_6$; **Chloride,** Fe_2Cl_6, and other haloids; **Sulphate,** $Fe_2(SO_4)_3$; **Acetate,** $Fe_2(C_2H_3O_2)_6$; **Chlorate,** $Fe_2(ClO_3)_6$; **Ferricyanide,** $Fe_2(Fe(CN)_6)_2$.

Insoluble Compounds.—Ferrous Oxide, FeO, black, dissolves in acids to ferrous salts.

Ferric Oxide, Fe_2O_3, hematite, specular iron ore, steel gray in native crystals, reddish brown in powder; dissolves with difficulty in HCl, HNO_3, H_2SO_4 to ferric salts.

Ferroso-Ferric Oxide, Fe_3O_4, magnetite, is a black, magnetic substance, soluble in HCl to a mixture of both chlorides; in aqua regia to ferric chloride, Fe_2Cl_6.

Ferrous Hydroxide, $Fe(OH)_2$, white, is precipitated from solutions of ferrous salts by alkaline hydroxides. It rapidly changes, first to a dirty green, from formation of ferroso-ferric hydroxide, $Fe_3(OH)_8$, and finally to reddish-brown, $Fe_2(OH)_6$. NH_4Cl prevents entirely the precipitation by NH_4OH, and partially that by KOH and NaOH. The precipitate dissolves readily in acids.

Ferric Hydroxide, $Fe_2(OH)_6$, red-brown, is precipitated from solutions of ferric salts by alkaline hydroxides. It is insoluble in NH_4 salts, readily soluble in acids.

Ferrous Sulphide, FeS, black, is precipitated from solutions of both ferrous and ferric salts by $(NH_4)_2S$. Exposed to air, it rapidly oxidizes to soluble $FeSO_4$. The precipitate is soluble in HCl and HNO_3.

H_2S does not produce any change in any ferrous solutions except the acetate. It reduces ferric salts to ferrous, with separation of S.

The reactions of the cyanogen compounds, phosphate and acetate, will be found in Acid Analysis.

ALUMINIUM (Al).—27.

A tin-white, lustrous metal, sonorous, very malleable and ductile. Sp. Gr. 2.58. Its hardness varies between that of silver and that of soft iron. Its tenacity is about that of copper. It melts at 700°. It is an excellent conductor of heat and electricity. Pure Al does not oxidize in air. It is readily soluble in HCl and in solutions of KOH and NaOH; soluble also in hot HNO_3 and H_2SO_4.

Soluble Compounds.—Chloride, Al_2Cl_6, a deliquescent, unstable substance. **Bromide,** Al_2Br_6, and **Iodide,** Al_2I_6; **Nitrate,** $Al_2(NO_3)_6$; **Sulphate,** $Al_2(SO_4)_3$; **Acetate,** $Al_2(C_2H_3O_2)_6$.

Alums.—The name alum is given to a large class of double salts, sulphates and selenates, of an alkali metal with Al, Cr, Fe, or Mn. They are all soluble in water, much more readily in hot than in cold. Ordinary alum is $K_2Al_2(SO_4)_4$.

Insoluble Compounds.—Oxide, Al_2O_3, alumina, forms colorless crystals or a white amorphous powder, soluble in acids

and alkaline hydroxides. Ignited Al_2O_3 is insoluble in water and in acids, but is made soluble in water by conversion to aluminates, *e. g.*, $Na_2Al_2O_4$, by fusion with $KHSO_4$, or Na_2CO_3 and KNO_3. It is found native as corundum, sapphire, and Oriental topaz and amethyst, etc.

Hydroxide, $Al_2(OH)_6$, precipitated as a grayish-white, gelatinous mass by alkaline hydroxides, carbonates and sulphides; completely soluble as aluminate in excess of NaOH and KOH, partly, in excess of NH_4OH. The presence of NH_4Cl and heating promote precipitation by NH_4OH.

CHROMIUM (Cr).—52.3.

A rare metal, whose properties have not been well determined. Its principal use is in hardening steel. It is both acid- and base-forming.

Soluble Compounds.—Chromic Chloride, Cr_2Cl_6, and other haloids; **Nitrate,** $Cr_2(NO_3)_6$; **Acetate,** $Cr_2(C_2H_3O_2)_6$; **Sulphate,** $Cr_2(SO_4)^8$; **Chrome Alum,** $K_2Cr_2(SO_4)_4$. All chromic compounds are green or violet, giving green or violet solutions. The violet solutions turn green on heating.

"Anhydrous Chromic Acid," CrO_3, scarlet acicular crystals, prepared by treating $K_2Cr_2O_7$ with concentrated H_2SO_4. It is a powerful oxidizing agent. Its solution in water is supposed to be chromic acid, H_2CrO_4. Solutions of chromates are decomposed by H_2S, being converted into chromic salts, from which Cr is precipitated along with the bases of Group III. (For reactions of chromic acid, see Acid Analysis.)

Insoluble Compounds.—Chromic Oxide, Cr_2O_3, green, soluble before ignition in most mineral acids, giving chromic salts; after ignition it is insoluble, but is made soluble in water by fusion with $KHSO_4$, or Na_2CO_3 and KNO_3, by change to chromates.

Hydroxide, $Cr_2(OH)_6$, bluish-green, precipitated by alkaline hydroxides, carbonates, and sulphides. Excess of KOH or NaOH dissolves the precipitate in the cold, but it is thrown down again on boiling. NH_4OH dissolves it slightly in the cold, scarcely at all when hot. $Cr_2(OH)_6$ is soluble in acids.

Explanation of Table V.

1. The Group reagent is $(NH_4)_2S$:

$Ni(NO_3)_2 + (NH_4)_2S = NiS + 2NH_4NO_3$ (same for Co, Mn, Zn).
$FeCl_2 + (NH_4)_2S = FeS + 2NH_4Cl$.
$Al_2(NO_3)_6 + 3(NH_4)_2S + 6H_2O =$
$Al_2(OH)_6 + 6NH_4NO_3 + 3H_2S$ (same for Cr).

In continued analysis, iron is now present only in the ferrous condition. (See Group IV, A, No. 1; Fresenius, par. 111, 3.)

Al and Cr are thrown down as hydroxides, sulphides of these metals not being formed in the wet way.

NH_4OH is added to render the solution alkaline. It tends to precipitate hydroxides of several members of the Group, but only $Al_2(OH)_6$, $Cr_2(OH)_6$, and $Fe_2(OH)_6$, in case ferric iron be present, are permanent, some of the other hydroxides dissolving in excess of the reagent, and the rest in NH_4Cl, which also favors precipitation of $Al_2(OH)_6$ and $Cr_2(OH)_6$. Moreover,

NH_4OH would precipitate $Mg(OH)_2$, partly at least, lessening delicacy of test for Mg in next group. NH_4Cl prevents this, forming with $Mg(OH)_2$ a soluble double salt:

$$Mg(OH)_2 + 4NH_4Cl = (NH_4Cl)_2MgCl_2 + 2NH_4OH.$$

Boiling aids precipitation and filtration. *Rapid filtration*, by aid of filter pump, prevents oxidation of sulphides to soluble sulphates.

2. The filtrate often appears dark, from presence of NiS, which is somewhat soluble in $(NH_4)_2S$, especially if the latter contain much free NH_3. *Boiling* causes NiS to separate from the filtrate, when it may be added to precipitate.

In any case, a few drops dilute HCl should be added to the filtrate to decompose $(NH_4)_2S$, and the whole evaporated and concentrated for Group III.

3. HCl should be *cold dilute*, to prevent solution of NiS and CoS.

$$FeS + 2HCl = FeCl_2 + H_2S \text{ (same for Mn and Zn).}$$
$$Al_2(OH)_6 + 6HCl = Al_2Cl_6 + 6H_2O \text{ (same for Cr).}$$

4. **Bead reactions for Ni:**

Oxidizing flame: $NiO + Na_2B_4O_7 = NiB_2O_4 + Na_2B_2O_4$.
Reducing flame: $NiB_2O_4 + C = Ni + CO + B_2O_3$.

In the reducing flame the color fades to a turbid gray from reduced metal, and finally disappears.

Bead reactions for Co:

Both flames: $CoO + Na_2B_4O_7 = CoB_2O_4 + Na_2B_2O_4$.

Presence of Cu, Fe, Mn, or Ni may obscure Co blue at first, but it will appear in the reducing flame.

The test here given for Ni in presence of Co depends on the oxidation of $Ni(OH)_2$ to $Ni_2(OH)_6$ by Br in presence of NaOH. Very little aqua regia should be used to dissolve the sulphides, to avoid necessity of using a great deal of NaOH to neutralize.

Reactions with Aqua Regia:

$$NiS + 2Cl = NiCl_2 + S \text{ (same for Co).}$$

From this solution, NaOH in excess precipitates both $Ni(OH)_2$ and $Co(OH)_2$:

$$NiCl_2 + 2NaOH = Ni(OH)_2 + 2NaCl \text{ (same for Co).}$$

Both precipitates dissolve in excess of KCN:

$$Ni(OH)_2 + 4KCN = Ni(CN)_2(KCN)_2 + 2KOH \text{ (same for Co).}$$

When this solution is rendered alkaline by NaOH, the Ni salt is converted into $Ni(OH)_2$. This is oxidized by Br:

$$3Ni(OH)_2 + 2Br = Ni_2(OH)_6 + NiBr_2.$$

The Co remains in solution as a potassium cobalticyanide. (See Fresenius, par. 108, 10; 109, 10; Prescott, par. 268, 281).

5. Boiling with HNO_3 oxidizes $FeCl_2$ to Fe_2Cl_6, insuring precipitation by NH_4OH in presence of NH_4Cl:

$$6FeCl_2 + 8HNO_3 = 2Fe_2Cl_6 + Fe_2(NO_3)_6 + 2NO + 4H_2O.$$

Very little HNO_3 must be used, and boiling must be very brief, to prevent raising Mn to manganic state, to be precipitated as hydroxide with hydroxides of Al, Cr, and Fe.

NH_4Cl dissolves $Mn(OH)_2$, and promotes precipitation of $Al_2(OH)_6$; *excess* of NH_4OH dissolves $Zn(OH)_2$:

$$Fe_2Cl_6 + 6NH_4OH = Fe_2(OH)_6 + 6NH_4Cl \text{ (same for Al and Cr).}$$

TABLE V.—ANALYSIS OF GROUP III.—A.

If the solution be an acid solution, test for phosphates and oxalates first, and if they be present use Table VI.
Co, Ni, Mn, Zn, Fe, Al, Cr.

1. To the filtrate from Group IV, or to the solution containing only Groups III—I, add **NH_4Cl, NH_4OH** in excess, heat to boiling, and add **$(NH_4)_2S$.** Filter rapidly, keeping the precipitate covered as much as possible with the liquid.

2. **Filtrate.** Groups II and I. Evaporate to half its bulk, add a few drops dil. HCl, and filter off any precipitated S. Reserve to test for Groups II and I.

3. **Precipitate.** CoS, NiS, MnS, ZnS, FeS, $Al_2(OH)_6$, $Cr_2(OH)_6$. Wash with hot water containing a little **$(NH_4)_2S$.** Transfer to an evaporating dish; treat with cold dilute **HCl,** and filter.

4. **Residue.** CoS, NiS. Test the residue on the filter for Co with **borax bead.** A blue bead indicates Co. A pale yellow bead in outer flame fading in inner flame indicates Ni. If the bead gives the Co reactions, test the residue for Ni by dissolving it in a little **aqua regia** and then precipitating the hydroxides of Co and Ni with **NaOH** in excess. Filter, and dissolve the precipitate in a small amount of a concentrated solution of **KCN.** To the dissolved cyanides add three times their bulk of **NaOH,** then **bromine water,** drop by drop, without disturbing liquid. A black ring ppt., $Ni_2(OH)_6$, indicates Ni.

5. **Solution.** $MnCl_2$, $ZnCl_2$, $FeCl_2$, Al_2Cl_6, Cr_2Cl_6. Add a few drops of strong **HNO_3,** and boil for a few minutes; then add **NH_4Cl, NH_4OH** in excess, let stand, and filter.

6. **Filtrate.** $MnCl_2$, $ZnCl_2$. Add **NaOH,** heat, and filter.

7. **Precipitate.** $Al_2(OH)_6$, $Cr_2(OH)_6$, $Fe_2(OH)_6$. Wash, dry, fuse on Pt foil with **Na_2CO_3** and **KNO_3,** boil fused mass in water, and filter. A blue-green coloration on foil indicates Mn.

8. **Precipitate.** $Mn(OH)_2$, flesh-colored, indicates Mn. Confirm by fusing with **KNO_3** and **Na_2CO_3.** "Peacock-blue." Mn.

9. **Filtrate.** Na_2ZnO_2. Add **$HC_2H_3O_2$** in excess, then **H_2S.** White ppt., ZnS, indicates Zn.

10. **Residue.** Fe_2O_3, brown, indicates Fe. Test the original solution for ferrous and ferric forms.*

11. **Solution.** $Na_2Al_2O_4$, K_2CrO_4, Na_2CrO_4. Yellow color of solution indicates Cr. Divide the solution into three parts.

12. (A) Add **NH_4Cl** and heat. White ppt. on standing, $Al_2(OH)_6$, indicates Al.

(B) Acidify with **HNO_3,** add **NH_4Cl** and **NH_4OH.** White ppt. after standing, $Al_2(OH)_6$, indicates Al.

13. (C) Acidify with **$HC_2H_3O_2$,** add **$Pb(C_2H_3O_2)_2$.** A yellow ppt., $PbCrO_4$, indicates Cr.

*A ferrocyanide with ferric salts gives deep blue precipitate. A ferricyanide with ferrous salts gives deep blue precipitate. A thiocyanate with ferric salts gives blood-red coloration.

6. Excess of NaOH dissolves $Zn(OH)_2$ as sodium zincate, precipitating Mn $(OH)_2$:

$$ZnCl_2 + 2NaOH = Zn(OH)_2 + 2NaCl.$$
$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O.$$
$$MnCl_2 + 2NaOH = Mn(OH)_2 + 2NaCl.$$
$$2Mn(OH)_2 + O \text{ (from air)} = Mn_2O_2(OH)_2 + H_2O.$$

7. The dried precipitate may be collected by burning the filter over a mortar.

The fusion converts $Cr_2(OH)_6$ into soluble alkaline chromates, to give tests for chromic acid.

$Al_2(OH)_6$ is converted into aluminates, while the heat changes $Fe_2(OH)_6$ to Fe_2O_3:

$$Cr_2(OH)_6 + 2KNO_3 + Na_2CO_3 = Na_2CrO_4 + K_2CrO_4 + 2NO + CO_2 + 3H_2O.$$
$$2Al_2(OH)_6 + 2KNO_3 + Na_2CO_3 = K_2Al_2O_4 + Na_2Al_2O_4 + 2NO + CO_2 + 3O + 6H_2O.$$
$$Fe_2(OH)_6 = Fe_2O_3 + 3H_2O.$$

Should traces of Mn have been thrown down with the hydroxides, fused mass will have characteristic color of manganates, "peacock green."

All dissolve in water except Fe_2O_3. The chromates color the solution yellow.

8. The fusion converts $Mn(OH)_2$ into sodium and potassium manganates:

$$3Mn(OH)_2 + 4KNO_3 + Na_2CO_3 = 2K_2MnO_4 + Na_2MnO_4 + 4NO + CO_2 + 3H_2O.$$

9. $HC_2H_3O_2$ is added to form $Zn(C_2H_3O_2)_2$, since H_2S will completely precipitate ZnS only from the acetate:

$$Na_2ZnO_2 + 4HC_2H_3O_2 = Zn(C_2H_3O_2)_2 + 2NaC_2H_3O_2 + 2H_2O.$$
$$Zn(C_2H_3O_2)_2 + H_2S = ZnS + 2HC_2H_3O_2.$$

If Fe has not been entirely removed, its black sulphide will interfere with Zn test.

10. Owing to the continual oxidation and reduction of iron compounds in the course of analysis, it is impossible to determine at this stage whether iron existed originally in the ferrous or ferric state. Consequently, the original solution must be tested for both forms.

Fe salts with $K_3Fe(CN)_6$ (ferricyanide):

$$3FeSO_4 + 2K_3Fe(CN)_6 = Fe_3(Fe(CN)_6)_2 + 3K_2SO_4.$$

Fe_2 salts with KSCN (thiocyanate):

$$Fe_2Cl_6 + 6KSCN = Fe_2(SCN)_6 + 6KCl.$$

12. **For Al:**

(A) $$Na_2Al_2O_4 + 2NH_4Cl + 4H_2O = Al_2(OH)_6 + 2NaCl + 2NH_4OH.$$

(B) $$NH_4OH + HNO_3 = NH_4NO_3 + H_2O.$$
$$Na_2Al_2O_4 + 2NH_4NO_3 + 4H_2O = Al_2(OH)_6 + 2NaNO_3 + 2NH_4OH.$$

13. Before testing for Cr, all carbonates must be removed, else, on adding $Pb(C_2H_3O_2)_2$, $Pb(CO_3)_2(OH)_2$, insoluble, would be formed. Hence addition of $HC_2H_3O_2$.

$$Na_2CrO_4 + Pb(C_2H_3O_2)_2 = PbCrO_4 + 2NaC_2H_3O_2.$$

TABLE VI.—ANALYSIS OF GROUP III.—B.

Co, Ni, Mn, Zn, Fe, Al, Cr; phosphates, oxalates, etc., of Group II.

1. To the filtrate from Group IV, or to the solution containing only Groups III–I, add **NH_4Cl, NH_4OH** in excess, heat to boiling, add **$(NH_4)_2S$.** Filter rapidly, keeping the precipitate covered with the liquid as much as possible.

2. Filtrate. Groups II and I. Evaporate to half its bulk, add a few drops dil. **HCl,** filter off any precipitated S. Reserve to test for Groups II and I.

3. Precipitate. CoS, NiS, MnS, ZnS, FeS, $Al_2(OH)_6$, $Cr_2(OH)_6$; phosphates, oxalates, etc., of Ba, Sr, Ca, Mg. Wash with hot water containing a little **$(NH_4)_2S$.** Treat with cold dil. **HCl,** and filter.

4. Residue. CoS, NiS, SiO_2. Test the residue on the filter with bead of "microcosmic salt." Skeleton, SiO_2; a blue bead indicates Co; a pale yellow bead in outer flame, fading in inner flame, indicates Ni.

Test for Ni as directed in Table V, 4.

5. Solution. $MnCl_2$, $ZnCl_2$, $FeCl_2$, Al_2Cl_6; $BaCl_2$, $SrCl_2$, $CaCl_2$, $MgCl_2$; H_3PO_4, $H_2C_2O_4$, etc. Divide into two parts, A and B.

To A (a small part) add dil. **H_2SO_4** and heat; $BaSO_4$, $SrSO_4$, and some $CaSO_4$ are precipitated. Examine ppt. with spectroscope, or boil with **Na_2CO_3;** filter, wash ppt., and dissolve in dil. **HCl;** evaporate solution, add water, and test for Ba, Sr, and Ca by Table VII. To filtrate, after adding H_2SO_4, add alcohol, **C_2H_5OH,** in excess. White ppt., $CaSO_4$, indicates Ca.

To B add cautiously **Fe_2Cl_6** until a drop of **NH_4OH** gives a yellowish ppt. Filter off precipitated $Fe_2(PO_4)_2$, and to filtrate add a few drops conc. **HNO_3;** boil, add **NH_4Cl, NH_4OH** in excess, let stand, and filter.

6. Filtrate. $MnCl_2$, $ZnCl_2$, $BaCl_2$, $SrCl_2$, $CaCl_2$, $MgCl_2$. Test for Mn and Zn as in Table V, 6. After removing Mn and Zn, add dil. **H_2SO_4;** heat, filter off precipitated $BaSO_4$ and $SrSO_4$; to filtrate add **NH_4Cl, NH_4OH,** and **$(NH_4)_2C_2O_4$;** filter off precipitated CaC_2O_4, and test for Mg as in Table VII, 2.

7. Precipitate. $Al_2(OH)_6$, $Cr_2(OH)_6$, $Fe_2(OH)_6$. Test for Al and Cr as in Table V, 7. Test original solution for Fe, — ferrous and ferric forms.

Explanation of Table VI.

The phosphates, oxalates, and salts of other acids of Group I, B, with bases of Group II, dissolve in acids, but are insoluble in alkalies. Hence, if these salts are present, they will be precipitated along with bases of Group III, on addition of NH_4OH. Therefore, if the original solution be an acid one, it must be examined for phosphoric and oxalic acids, and if they be found, Table VI must be followed in place of Table V.

4. SiO_2 remains with the sulphides of Co and Ni. It may be tested for as in Acid Analysis, Group I, A, No. 7, after dissolving CoS and NiS in aqua regia.

5. The tests for Ba, Sr, and Ca are explained in Group II. Mg cannot be found until H_3PO_4 has been removed. This may be most conveniently done by adding Fe_2Cl_6, as in Acid Analysis, Group I, B, No. 1. A yellowish precipitate, $Fe_2(OH)_6$, with NH_4OH, shows that the phosphoric acid has been entirely removed. Of course, the tests for Fe and Fe_2 must be made in the original solution.

6. Before testing for Mg, Ba and Sr are removed by the usual methods.

PROPERTIES OF GROUP II.

BARIUM (Ba).—137.

Variously described as a silver-white and golden-yellow metal, malleable and ductile. Sp. Gr. 3.5 to 4. It oxidizes rapidly in air, and decomposes cold water.

Soluble Compounds.—**Nitrate,** $Ba(NO_3)_2$; **Chloride,** $BaCl_2$, and other haloids; **Sulphide,** BaS; **Acetate,** $Ba(C_2H_3O_2)_2$; **Chlorate,** $Ba(ClO_3)_2$. The nitrate and chloride are insoluble in their respective acids.

Insoluble Compounds.—**Barium Monoxide,** BaO, baryta, is a grayish powder, very poisonous; soluble in water, combining chemically to form the hydroxide, $Ba(OH)_2$.

Barium Peroxide, BaO_2, is a white powder, used as a source of oxygen, and in the manufacture of hydrogen peroxide, H_2O_2. The latter is formed by treating BaO_2 with dilute acids at reduced temperatures.

Hydroxide, $Ba(OH)_2$, "caustic baryta," is a white substance, dissolving in 20 parts cold, or 2 parts hot, water. This solution, baryta water, corresponding to lime water, is an alkaline, caustic liquid. $Ba(OH)_2$ is precipitated by alkaline hydroxides only from very concentrated solutions.

Sulphate, $BaSO_4$, white, is precipitated even from very dilute solutions by H_2SO_4 and all soluble sulphates. It forms immediately in the cold, which serves to distinguish Ba from Sr. From dilute solutions the precipitate is very finely divided, and hence very difficult to filter. The reaction with sulphates is most frequently used as a test for Ba, and also for H_2SO_4.

Carbonate, $BaCO_3$, white, is precipitated by alkaline carbonates. It is perceptibly soluble in NH_4Cl, and freely soluble in acids.

Chromate, $BaCrO_4$, yellow, is precipitated by both chromates and dichromates. It is readily soluble in mineral acids, scarcely soluble in $HC_2H_3O_2$. NH_4OH reprecipitates it from solution in acids.

Barium compounds impart to the colorless Bunsen flame a yellowish-green color. The spectrum is characterized by a series of green lines.

For further details concerning reactions of Ba salts, see Acid Analysis, Group I.

STRONTIUM (Sr).—87.5.

A yellowish metal, harder than Pb, malleable and ductile. Sp. Gr. 2.4. It oxidizes in air, and decomposes water with violence. It is soluble in acids.

Soluble Compounds.—**Nitrate,** $Sr(NO_3)_2$; **Chloride,** $SrCl_2$, and other haloids; **Sulphide,** SrS; **Chlorate,** $Sr(ClO_3)_2$; **Acetate,** $Sr(C_2H_3O_2)_2$.

Insoluble Compounds.—There is a very close resemblance between the compounds of Sr and Ba. **Strontium Hydroxide** is somewhat less soluble in water than the corresponding Ba compound; the **Carbonate** is less soluble in NH_4Cl; the **Chromate** is scarcely precipitated at all by $K_2Cr_2O_7$, though precipitated from strong solution by K_2CrO_4; the **Sulphate** is more soluble in water, and precipitated more slowly than that of Ba, usually requiring the aid of heat.

The color imparted to the Bunsen flame is a bright crimson. The most distinctive mark of the spectrum is the blue line, Sr δ.

CALCIUM (Ca).—40.

A clear, yellowish-white, lustrous metal, malleable and ductile. Sp. Gr. 1.57. Like Ba and Sr it oxidizes in moist air, and decomposes water.

Soluble Compounds.—Same as for Ba and Sr.

Insoluble Compounds.—**Hydroxide,** $Ca(OH)_2$, "slaked lime," is much less soluble in water than the corresponding Ba and Sr compounds; **Sulphate,** $CaSO_4$, is more soluble, its solution being used to effect the detection of Ba and Sr in presence of Ca; **Chromate,** $CaCrO_4$, is not precipitated by either K_2CrO_4 or $K_2Cr_2O_7$; **Carbonate,** $CaCO_3$, is somewhat soluble in NH_4Cl, freely soluble in acids.

Ca is usually identified as **Oxalate,** CaC_2O_4, by precipitation with $(NH_4)_2C_2O_4$, best in presence of NH_4OH. The precipitate is freely soluble in HCl and HNO_3. This test supposes the complete removal of Ba and Sr, as their oxalates are formed under precisely similar conditions.

The Bunsen flame is colored yellowish-red by Ca compounds, the reaction being most pronounced with $CaCl_2$. The spectrum contains two characteristic lines, a bright green, Ca β, and a very bright orange, Ca α.

MAGNESIUM (Mg).—24.

A silver-white metal, very lustrous; moderately hard; malleable and ductile, not very tenacious. Sp. Gr. 1.75. It does not oxidize in dry air, but becomes coated with oxide in ordinary air; heated in air, it burns to MgO, with a bright white light very rich in actinic rays. It does not decompose cold water at all, and decomposes hot water only slowly. It dissolves readily in dilute acids.

Soluble Compounds.—**Nitrate,** $Mg(NO_3)_2$; **Chloride,** $MgCl_2$, and other haloids; **Sulphate,** $MgSO_4 . 7H_2O$, "Epsom salts;" **Chlorate,** $Mg(ClO_3)_2$; **Acetate,** $Mg(C_2H_3O_2)_2$; all are deliquescent, except $MgSO_4$, which effloresces somewhat. In solution, Mg salts have a nauseating taste.

Insoluble Compounds.—**Oxide,** MgO, white, "magnesia," formed by igniting the metal or the carbonate and most other salts. It is soluble in dilute acids.

Hydroxide, $Mg(OH)_2$, white, precipitated by KOH and NaOH, partially by NH_4OH, the remaining part going into solution in the NH_4Cl or other NH_4 salt formed in the reaction. The precipitate is entirely prevented by the addition of an NH_4 salt. It dissolves also in dilute acids.

Carbonate.—Mg forms, besides the normal carbonate, $MgCO_3$, various basic salts and double carbonates, for a description of which, see Watts's Dictionary, 2d edition, Vol. I., p. 699; also, Prescott, par. 77; Fresenius, par. 98, 6 and 7. $(NH_4)_2CO_3$ fails to precipitate Mg salts, owing to formation of a soluble double salt, especially in presence of NH_4Cl. (See Working Scheme.)

TABLE VII.—ANALYSIS OF GROUP II.

Ba, Sr, Ca, Mg.

1. To the filtrate from Group III, concentrated by evaporation, after addition of a few drops dil. HCl, and cleared by filtering, or to the solution containing only Groups II and I, add **NH_4Cl, NH_4OH**; heat gently, add **$(NH_4)_2CO_3$**, and filter.

2. **Filtrate.** Mg remains in solution with salts of Group I. To a small portion add dilute **H_2SO_4**, and filter, if Ba has been found; then **NH_4Cl, NH_4OH** and **$(NH_4)_2C_2O_4$**, and filter, if Ca has been found; then **Na_2HPO_4**. A white ppt. NH_4MgPO_4, shows presence of Mg. Reserve the remainder of the filtrate to test for Group I.

3. **Precipitate.** $BaCO_3$, $SrCO_3$, $CaCO_3$. Wash well with cold water and dissolve in **$HC_2H_3O_2$**.
Solution. $Ba(C_2H_3O_2)_2$, $Sr(C_2H_3O_2)_2$, $Ca(C_2H_3O_2)_2$. To a small portion add **$CaSO_4$**; immediate white ppt. indicates Ba; white ppt., tardy or appearing only on heating, indicates Sr. If Ba is absent, but Sr present, skip to 7 (B); if Ba and Sr are both absent, skip to 9; if Ba is present, add to the rest of the solution **$K_2Cr_2O_7$**; heat, and filter. (Barter, $(NH_4)_2CrO_4$)

4. **Precipitate.** Yellow $BaCrO_4$. Reject.

5. **Filtrate.** $Ca(C_2H_3O_2)_2$, $Sr(C_2H_3O_2)_2$. To the filtrate add **NH_4OH** in excess; heat, add **$(NH_4)_2CO_3$**, and filter.

6. **Filtrate.** Reject.

7. (A) **Precipitate.** $SrCO_3$, $CaCO_3$. Wash the ppt. until wash water runs through clear, and dissolve in **$HC_2H_3O_2$**.
(B) **Solution.** $Sr(C_2H_3O_2)_2$, $Ca(C_2H_3O_2)_2$. Add to a small portion **$CaSO_4$**, and heat; white ppt., on standing, indicates Sr. If Sr is absent, skip to 9; if Sr is present, add to rest of solution dil. **H_2SO_4**, boil, allow to stand for some time, and filter.

8. **Precipitate.** $SrSO_4$. Reject.

9. **Filtrate.** $Ca(C_2H_3O_2)_2$. Add **NH_4OH** in slight excess, and then **$(NH_4)_2C_2O_4$**; a white ppt., CaC_2O_4, indicates Ca.

Explanation of Table VII.

1. HCl decomposes $(NH_4)_2S_x$ from last group:

$$2HCl + (NH_4)_2S_x = 2NH_4Cl + H_2S + (x-1)S.$$

NH_4Cl keeps up Mg, as in last Group. Care should be taken not to add too much, as it tends to dissolve a trace of $CaCO_3$, and more than a trace of $BaCO_3$. (See Fresenius, par. 99.) In continued analysis, enough will come over from Group III.

NH_4OH promotes precipitation of carbonates, and prevents formation of bicarbonates.

$(NH_4)_2CO_3$ is used in preference to fixed alkali carbonates, as the metals of the latter are to be tested for later on. With Mg a soluble double carbonate is formed.

Reactions:

$$Mg(NO_3)_2 + 2(NH_4)_2CO_3 = MgCO_3 . (NH_4)_2CO_3 \text{ (soluble)} + 2NH_4NO_3.$$

$$Ba(NO_3)_2 + (NH_4)_2CO_3 = BaCO_3 + 2NH_4NO_3 \text{ (same for Sr and Ca).}$$

Heating promotes precipitation and filtering. Too great heat interferes.

3. The precipitated carbonates are *washed* to free them from NH_4OH and $(NH_4)_2CO_3$, in neutralizing which $HC_2H_3O_2$ would be wasted and the solution diluted. The carbonates dissolve easily in dilute HCl or HNO_3, but $HC_2H_3O_2$ is preferred on account of the lesser solubility of $BaCrO_4$ in that acid. Even $HC_2H_3O_2$ dissolves $BaCrO_4$ somewhat. Hence as little as possible should be used.

Reaction:

$$BaCO_3 + 2HC_2H_3O_2 = Ba(C_2H_3O_2)_2 + CO_2 + H_2O$$

(same for Sr and Ca).

The $CaSO_4$ test distinguishes Ba far more readily than the $K_2Cr_2O_7$ test, owing to the color of the latter reagent, but cannot be used to remove Ba, as it also precipitates Sr, and introduces Ca.

With $CaSO_4$:

$$Ba(C_2H_3O_2)_2 + CaSO_4 = BaSO_4 + Ca(C_2H_3O_2)_2 \text{ (same for Sr).}$$

With $K_2Cr_2O_7$:

$$Ba(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = BaCrO_4 + H_2CrO_4 + 2KC_2H_3O_2.$$

5 and 7 (A). In order to remove the color of $K_2Cr_2O_7$, the carbonates are reproduced, and the precipitate washed and redissolved in $HC_2H_3O_2$. When, in the proved absence of Ba, $K_2Cr_2O_7$ has not been added, these operations are unnecessary.

7 (B). H_2SO_4 does not furnish a sufficiently accurate test for Sr, as it also throws down some Ca.

$CaSO_4$ is therefore used to test for Sr, and H_2SO_4 to remove it. Sufficient $CaSO_4$ will remain in solution for the oxalate test:

$$Sr(C_2H_3O_2)_2 + H_2SO_4 = SrSO_4 + 2HC_2H_3O_2.$$

9. Ca is identified as CaC_2O_4. Free H_2SO_4 interferes with the

test. It is neutralized with NH_4OH. Then, on addition of $(NH_4)_2C_2O_4$:

$$CaSO_4 + (NH_4)_2C_2O_4 = CaC_2O_4 + (NH_4)_2SO_4.$$

Ba, Sr, and Ca are easily recognized in the spectroscope, but the method here given is preferred as being more instructive.

2. Before testing for Mg, assurance must be had that the filtrate contains no Ba or Ca, since those metals also give a white precipitate with Na_2HPO_4. H_2SO_4 is applied to a small portion. If a precipitate forms, $BaSO_4$, it is filtered off, and the filtrate tested for traces of Ca by $(NH_4)_2C_2O_4$ and NH_4OH. NH_4Cl is added as usual to prevent loss of Mg. The last filtrate is tested for Mg by Na_2HPO_4.

Reaction for Mg test:

$$MgCO_3(NH_4)_2CO_3 + Na_2HPO_4 + NH_4OH = Na_2CO_3 + (NH_4)_2CO_3 + NH_4MgPO_4 + H_2O.$$

From dilute solution the precipitate settles very slowly in crystals. Stirring with a glass rod against the sides of the test tube causes the crystals to form along the marks made.

The remainder of the filtrate is reserved for Group I.

PROPERTIES OF GROUP I.

Potassium, K, 39; **Sodium,** Na, 23; **Lithium,** Li, 7; **Ammonium,** NH_4.

K, Na, and Li are soft, wax-like bodies at ordinary temperatures, oxidizing in ordinary air. They are lighter than water, and decompose it, with evolution of part of the hydrogen, the remaining portion entering into combination with the metal and oxygen to form the hydroxides of the metals. NH_4 is an hypothetical metal, never having been separated from its supposed compounds.

All the important compounds of the alkali metals are soluble in water. Hence these metals are not precipitated by the ordinary reagents. They are usually recognized by the colors they impart to the Bunsen flame, or by their spectra. The following reactions are of some importance in analysis:

Potassium Platinic Chloride, $(KCl)_2PtCl_4$, yellow, crystalline, is precipitated by platinic chloride, $PtCl_4$, from not too dilute solutions of potassium compounds, preferably from the chloride. The solution must be neutral or acid.

Potassium Hydrogen Tartrate, $KHC_4H_4O_6$, white, is precipitated by tartaric acid, $H_2C_4H_4O_6$, or sodium hydrogen tartrate, $NaHC_4H_4O_6$, from somewhat concentrated solutions of potassium compounds. The precipitate is soluble in mineral acids and in alkalies. Hence the addition of tartaric acid to strong acid reaction is advisable.

Ammonium compounds react with both of the above reagents with results very similar to those obtained with potassium, and must, therefore, be removed by ignition, before applying tests for potassium.

Ammonium is usually detected by the liberation of NH_3 by the action of alkalies.

Nessler's Test for Ammonium.—The reagent is **Potassium Mercuric Iodide,** $(KI)_2HgI_2$, with potassium hydroxide, KOH. (For preparation, see Appendix.) The precipitate from NH_4 compounds is brown; in very dilute solutions, only a brownish coloration is had.

Reaction:

$$NH_4OH + 2(KI)_2HgI_2 + 3KOH = NHg_2I + 7KI + 4H_2O.$$

Lithium Phosphate, Li_3PO_4, white, is precipitated by Na_2HPO_4. The precipitate is formed best in a boiling solution.

TABLE VIII.—ANALYSIS OF GROUP I.

Na, K, Li, NH_4.

Evaporate to dryness the filtrate from Group II, after removing traces of Ba and Ca by H_2SO_4 and $(NH_4)_2C_2O_4$; moisten with **HCl** (since the chlorides, being most volatile, are best adapted for spectroscopic work), and test before the spectroscope. A yellow band indicates Na; a faint red band in the extreme red indicates K; a bright crimson band between the two indicates Li.

In the Bunsen flame, Na gives a yellow coloration; K, a violet coloration, overwhelmed by Na, but revealed by cobalt glass; Li, a crimson coloration.

NH_4 compounds are detected by the liberation of NH_3 by means of an **alkali.** The original solution is mixed with $Ca(OH)_2$, **NaOH,** or **KOH,** and the mixture heated. NH_3 given off may be recognized by its action on red litmus or on turmeric paper. Care must be taken to prevent the added alkali from affecting the paper. The reaction:

$$2NH_4NO_3 + Ca(OH)_2 = 2NH_3 + Ca(NO_3)_2 + 2H_2O.$$

PART II.—ACID ANALYSIS.

HAVING discovered what bases are contained in a given substance, it remains to determine in what forms of combination they exist; *i.e.*, with what acid radicals they are united to form salts. This is effected by testing for the various acid radicals.

The first step in Acid Analysis is to consider what acids form, with the bases found, salts soluble in the menstruum present; since, of course, it is useless to look for acids which form insoluble salts with any of the bases present. For example, if, in a water solution, Ag or Hg_2 has been found, HCl cannot possibly be present; if Pb, Ba, or Sr has been found, H_2SO_4 cannot be present; since, as we know, the chlorides in the first instance, and the sulphates in the second, are insoluble in water. Similarly in an acid solution—*i.e.*, in a solution containing only substances soluble in acids only—no acids need be looked for which form, with any of the bases found, salts soluble in water. Again, it must be remembered that no acid can be present which forms an insoluble salt with any one base found, even though the corresponding salts of all the other bases found be soluble. To illustrate, let us suppose that in a water solution, Ag and Ba have been found. We know that $BaCl_2$ dissolves in water. If, therefore, we consider Ba alone, we shall be led to test for HCl; but if we remember that AgCl is insoluble, we see at once that the Ba cannot exist as $BaCl_2$, since, in that case, AgCl would be formed, and fail to go into solution.

The indications with H_2SO_4, in the preliminary examination, will aid in still further limiting the number of acids to be tested for. For example, if no reddish-brown fumes were noticed, bromides can scarcely be present; if no violet color, iodides need not be tested for; if the reaction with NH_4OH was wanting, chlorides are excluded, etc. Still the analyst must not confide too much in the preliminary examination, as peculiar circumstances may prevent the indications. Mention is made here of these indications merely as a guide.

The next step is to examine whether any complications are likely to arise from the presence of the bases in solution, when the tests for acids are made. Thus, if Ag is present, $BaCl_2$ cannot be used as reagent, since it would precipitate AgCl; if Ba is present, $FeSO_4$ and H_2SO_4 cannot be used, since they would form insoluble $BaSO_4$. In general, it is necessary to remove all except Group I bases before testing for acids, both to guard against reactions between the bases in solution and the acid radicals of reagents, and because the tests suggested are most satisfactory when the acids are combined with Group I bases. The bases may, of course, be removed by the several Group reagents,

—HCl, H_2S, $(NH_4)_2S_x$, $(NH_4)_2CO_3$, Na_2HPO_4; but excess of some of these is rather difficult to expel, and, moreover, the presence of NH_4 salts in quantity is not desirable. If As is absent, all the bases may be conveniently removed by boiling or fusing with Na_2CO_3, excess of the reagent being afterwards carefully neutralized in the filtrate, to prevent formation of insoluble carbonates with the bases of reagents. Frequently, particular reagents may be used to advantage, while in some cases the difficulty may be obviated by a change of reagent. Thus, in the case of Ag, mentioned above, $Ba(NO_3)_2$ may be substituted for $BaCl_2$, the Ag being left in solution. Sometimes not even a change of reagent is necessary. The analyst will be able to form a correct judgment in all cases from his knowledge of the properties of the bodies he is dealing with.

Finally, the acid tests are applied. The Group reagents, $BaCl_2$ and $AgNO_3$, are first added, to determine what classes of acids are present, and then the special tests are applied, as directed in the Working Scheme.

GROUPING OF THE ACIDS.

Many authors divide the acids into two classes, *organic* and *inorganic*, or those which deposit carbon on ignition and those which do not; but as the more common organic acids may be conveniently classed for purposes of analysis with the inorganic acids, this division is not here taken into account.

Acids cannot be grouped as accurately as the bases, and no such consecutive scheme can be presented as has been done in the case of the bases, but the labor is somewhat shortened by the indications with certain reagents; viz., $BaCl_2$ and $AgNO_3$. The nonformation of a precipitate with one or both of these reagents proves at once the absence of a majority of the acids, while, should a precipitate form, its behavior with certain other reagents determines the course of the analysis.

In the following scheme the grouping is exhibited in tabular form, three Groups being recognized, as follows:

Group I comprises the acids precipitated by $BaCl_2$, and is subdivided into

A, or acids of which indications are had in the course of Basic Analysis; viz., the acids of As, from which As is precipitated by H_2S among the bases of Group IV; chromic, decomposed by H_2S, with formation of chromic salts, from which Cr is precipitated by NH_4OH and $(NH_4)_2S_x$ in Group III; sulphurous and thiosulphuric (hyposulphurous), decomposed by HCl with evolution of SO_2; carbonic, decomposed by HCl, with evolution of CO_2; silicic, from solutions of whose alkaline salts part of the acid separates on addition of HCl.

B, or acids not decomposed in course of Basic Analysis; viz., sulphuric, phosphoric, boric, oxalic, tartaric, hydrofluoric.

Group II comprises acids not precipitated by $BaCl_2$ but precipitated by $AGNO_3$, the Ag salts formed, except AgS, being insoluble in HNO_3 (distinction from Ag salts of acids of A); viz., hydrochloric, hydrobromic, hydriodic, hydrocyanic, ferricyanic, ferrocyanic, hydrosulphuric.

Group III comprises the acids not precipitated by the reagents of Groups I and II; viz., nitric, chloric, acetic.

(See Fresenius, par. 136, 137.)

TABLE IX.

Group.	I.		II.	III.
Reagent.	$BaCl_2$.		$AgNO_3$.	——
	A.	B.		
	M_2CrO_4, M_3AsO_3, H_3AsO_4, H_2SO_3, $H_2S_2O_3$, M_2CO_3, H_4SiO_4 — decomposed by **HCl** and H_2S in Basic Analysis.	H_2SO_4, H_3PO_4, H_3BO_3, $H_2C_2O_4$, $H_2C_4H_4O_6$, HF — not decomposed by **HCl** or H_2S.	HCl. HBr. HI. HCN. $H_4Fe(CN)_6$. $H_3Fe(CN)_6$. H_2S.	HNO_3. $HClO_3$. $HC_2H_3O_2$.

TABLE X.—ANALYSIS OF GROUP I., DIV. A.

M_2CrO_4, M_3AsO_3, H_3AsO_4, H_2SO_3, $H_2S_2O_3$, M_2CO_3, H_4SiO_4.

Indications of these acids will have been had in course of basic analysis or in preliminary examination.

Treat small portions of the original solution in each of the following ways:

1. M_2CrO_4, **Chromates.**	2. M_3AsO_3, **Arsenites.**	3. H_3AsO_4, **Arsenates.**	4. H_2SO_3, **Sulphites.**	5. $H_2S_2O_3$, **Thiosulphates.**	6. M_2CO_3, **Carbonates.**	7. H_4SiO_4, **Silicates.**
Acidify with $HC_2H_3O_2$, and add $Pb(C_2H_3O_2)_2$. Yellow ppt., $PbCrO_4$, indicates chromates. Confirmed by adding $AgNO_3$ to a neutral solution. Dark-red Ag_2CrO_4 is precipitated.	Acidify with **HCl**, heat, and add H_2S. An immediate yellow ppt. indicates arsenites. Confirmed by adding $AgNO_3$ to a neutral solution. Yellow Ag_3AsO_3 is precipitated. Distinguished from arsenates by giving, on boiling with $CuSO_4$ and **NaOH**, an orange-yellow ppt., $Cu_2(OH)_2$.	Acidify with **HCl**, heat, and add H_2S. A slow yellow ppt. indicates arsenates. Confirmed by adding $AgNO_3$ to a neutral solution. Brown Ag_3AsO_4 is precipitated. Distinguished from arsenites by giving a white ppt., $MgNH_4AsO_4$, with **"magnesia mixture."**	Add strong **HCl**. SO_2 gas given off, suffocating odor of burning S, indicates sulphites.	Add strong **HCl**. SO_2 gas given off, with a deposit of S, indicates thiosulphates. Confirmed by adding $Pb(C_2H_3O_2)_2$. A white ppt., PbS_2O_3, decomposing on boiling to black PbS.	Treat dry salt with dil. **HCl**. CO_2 gas, rendering lime water turbid, indicates carbonates.	Acidulate with **HCl**, evaporate to dryness on water bath, treat residue with **water** and **HCl**. SiO_2, a gritty powder, is left undissolved. Confirmed by bead of $NaNH_4HPO_4$, "microcosmic salt." "Skeleton bead" indicates silicates.

Explanation of Table X.

1. M_2CrO_4, Chromates.

Chromates need be looked for only when Cr has been found among the bases, as they are converted by H_2S in Group IV. into salts of chromium, from which the base is precipitated in Group III., as $Cr_2(OH)_6$. Hence, the mere discovery of Cr does not determine in what form it originally existed, whether as a base or as an acid. The original solution is, therefore, now to be tested with $Pb(C_2H_3O_2)_2$ in presence of $HC_2H_3O_2$, a yellow precipitate, $PbCrO_4$, proving presence of chromates, while chromic compounds give this precipitate only after fusion with KNO_3 and Na_2CO_3. The reactions of $PbCrO_4$ have been given in Group V., Basic Analysis.

The confirmatory test by $AgNO_3$ requires the solution to be neutral, because Ag_2CrO_4 dissolves in acids and some alkalies.

Reactions:

$$K_2CrO_4 + 2AgNO_3 = Ag_2CrO_4 + 2KNO_3.$$
$$K_2Cr_2O_7 + 2AgNO_3 = Ag_2CrO_4 + 2KNO_3 + CrO_3.$$

$BaCl_2$ gives $BaCrO_4$, yellow, soluble in HCl and HNO_3, insoluble in $HC_2H_3O_2$. (See Basic Analysis, Group II.)

2. M_3AsO_3, Arsenites.

For reactions with H_2S, see Basic Analysis, Group IV., Div. A, 1.

Confirmatory test with $AgNO_3$:

$$Na_3AsO_3 + 3AgNO_3 = Ag_3AsO_3 + 3NaNO_3.$$

The precipitate dissolves in acids and in NH_4OH; hence the solution must be neutral.

Confirmatory test with $CuSO_4$:

In neutral solutions, $CuSO_4$ precipitates $CuHAsO_3$, "Paris Green:"

$$Na_3AsO_3 + CuSO_4 + H_2O = CuHAsO_3 + NaOH + Na_2SO_4.$$

If, however, the arsenite solution be mixed with NaOH or KOH, previously to addition of $CuSO_4$, the As passes into solution as Na or K arsenate, and orange $Cu_2(OH)_2$, cuprous hydroxide, is precipitated:

$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4.$$
$$2Cu(OH)_2 + Na_3AsO_3 = Cu_2(OH)_2 + Na_3AsO_4 + H_2O.$$

3. H_3AsO_4, Arsenates.

For reactions with H_2S, see Basic Analysis, Group IV., Div. A, 1.

Confirmatory test with $AgNO_3$:

$$Na_3AsO_4 + 3AgNO_3 = Ag_3AsO_4 + 3NaNO_3.$$

Conditions and solubilities same as for Ag_3AsO_3.

"Magnesia mixture" consists of $MgSO_4$ and NH_4OH, with enough NH_4Cl to prevent precipitation of $Mg(OH)_2$.

Reaction:

$$MgSO_4 + NH_4OH + Na_3AsO_4 = MgNH_4AsO_4 + Na_2SO_4 + NaOH.$$

4. **H_2SO_3, Sulphites.**

With HCl, SO_2 is liberated without deposit of S (distinction from thiosulphates).

Reaction:

$$Na_2SO_3 + 2HCl = SO_2 + H_2O + 2NaCl.$$

Confirmatory test with $Pb(C_2H_3O_2)_2$:

$$Na_2SO_3 + Pb(C_2H_3O_2)_2 = PbSO_3 + 2NaC_2H_3O_2.$$

$BaCl_2$ gives white $BaSO_3$, soluble in dilute HCl. If to this solution aqua regia is added, $BaSO_4$ is precipitated:

$$Na_2SO_3 + BaCl_2 = BaSO_3 + 2NaCl.$$
$$BaSO_3 + 2HCl = BaCl_2 + H_2SO_3.$$
$$BaCl_2 + H_2SO_3 + 2Cl + H_2O = BaSO_4 + 4HCl.$$

5. **$H_2S_2O_3$, Thiosulphates.**

With HCl:

$$Na_2S_2O_3 + 2HCl = SO_2 + S + H_2O + 2NaCl.$$

Confirmatory test with $Pb(C_2H_3O_2)_2$:

$$Na_2S_2O_3 + Pb(C_2H_3O_2)_2 = PbS_2O_3 + 2NaC_2H_3O_2.$$
$$PbS_2O_3 + H_2O = PbS + H_2SO_4.$$

$BaCl_2$ gives BaS_2O_3, white.

$$Na_2S_2O_3 + BaCl_2 = BaS_2O_3 + 2NaCl.$$

Precipitate dissolves in acids, with residue of S.

$$BaS_2O_3 + 2HCl = SO_2 + S + H_2O + BaCl_2.$$

6. **M_2CO_3, Carbonates.**

$$M_2CO_3 + 2HCl = 2MCl + CO_2 + H_2O.$$
$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O.$$

$BaCl_2$ gives white $BaCO_3$, soluble in dilute acids. (See Basic Analysis, Group II.)

7. **H_4SiO_4, Silicates.**

As a rule, silicates will be found only in substances insoluble in water and acids, the alkaline silicates alone being soluble. These are decomposed by HCl (and all other acids), with separation of a gelatinous precipitate, probably H_4SiO_4. For the success of this test, the acid must be added slowly, whilst stirring the fluid, else the precipitate will not separate, the liberated acid going into solution in the HCl. As the solution is evaporated, and the HCl escapes, the silicic acid separates, and, on evaporation to dryness, is decomposed with a residue of SiO_2, insoluble in HCl. (See Fresenius, par. 150, 2; Prescott, par. 745.)

In the bead of "microcosmic salt" the bases contained in silicates dissolve, leaving SiO_2 undissolved as a skeleton of the original fragment.

Explanation of Table XI.

1. Acids of Group I, A, are removed by HCl and H_2S, as they also are precipitated by the Group reagent.

The solution is rendered neutral or slightly alkaline, to prevent solution of the Ba salts in acids.

Reactions:

$$M_2SO_4 + BaCl_2 = BaSO_4 + 2MCl.$$
$$2M_3PO_4 + 3BaCl_2 = Ba_3(PO_4)_2 + 6MCl.$$
$$M_2HPO_4 + BaCl_2 = BaHPO_4 + 2MCl.$$
$$M_2C_2O_4 + BaCl_2 = BaC_2O_4 + 2MCl.$$
$$2M_3BO_3 + 3BaCl_2 = Ba_3(BO_3)_2 + 6MCl.$$
$$2MF + BaCl_2 = BaF_2 + 2MCl.$$
$$M_2C_4H_4O_6 + BaCl_2 = BaC_4H_4O_6 + 2MCl.$$

2. On boiling the precipitate with dilute HCl, all the Ba salts dissolve, except $BaSO_4$, the acids, except H_2SO_4, being liberated; *e.g.*,

$$Ba_3(PO_4)_2 + 6HCl = 2H_3PO_4 + 3BaCl_2.$$

3. The insolubility of a Ba salt in HCl is distinctive for H_2SO_4 only when the HCl is very dilute, since concentrated HCl precipitates the reagent itself unchanged, the precipitate dissolving again on diluting with water.

4. NH_4OH reproduces the Ba salts. This reaction is not very reliable, as most of the Ba salts are somewhat soluble in the NH_4 salts formed.

5. **H_3PO_4, Phosphates.**

In aqueous solutions, phosphates are tested for by "magnesia mixture," just as in testing for Mg a phosphate was used:

$$Na_3PO_4 + MgSO_4 + NH_4OH = MgNH_4PO_4 + Na_2SO_4 + NaOH.$$
$$Na_2HPO_4 + MgSO_4 + NH_4OH = MgNH_4PO_4 + Na_2SO_4 + H_2O.$$

Presence of arsenic acid and arsenates interfere.

For composition of the yellow ammonium phosphomolybdate, see Fresenius, par. 142, 10, note; American Journal of Chemistry, Vol. III., pp. 324, *sq.* As the precipitate is somewhat soluble in the phosphate solution, the reagent must be added in excess; hence the direction about adding solution to reagent, and not *vice versa*. From very dilute solutions the precipitate separates only on standing for some time at about 40°. Arsenic and silicic acids should be removed, since they also, especially if the solution be heated above 40°, may give yellow precipitates. With phosphates, the liquid above the precipitate is colorless, while with arsenates and silicates, the liquid is yellow. (See Fresenius, par. 142, 10.)

The test by Fe_2Cl_6 is particularly adapted to the detection of phosphoric acid in combination with the metals of the alkaline earths. Excess of the reagent must be avoided, to prevent formation of red ferric acetate. Arsenic acid and arsenates interfere. (See Fresenius, par. 142, 9; par. 147.)

Reaction:

$$Ba_3(PO_4)_2 + Fe_2Cl_6 = Fe_2(PO_4)_2 + 3BaCl_2.$$

TABLE XI.—ANALYSIS OF GROUP I., DIV. B.

H_2SO_4, H_3PO_4, $H_2C_2O_4$, H_3BO_3, HF, $H_2C_4H_4O_6$.

1. Remove acids of Group I, A, by means of **H_2S**, and filter; boil filtrate and add **NH_4OH** and **$BaCl_2$**.

2. **Precipitate.** $BaSO_4$; $Ba_3(PO_4)_2$, $BaHPO_4$, etc.; BaC_2O_4, $Ba_3(BO_3)_2$, BaF_2, $BaC_4H_4O_6$. Add dilute **HCl**, boil, and filter.

3. **Residue.** $BaSO_4$ indicates H_2SO_4.

4. **Solution.** H_3PO_4, $H_2C_2O_4$, H_3BO_3, HF, $H_2C_4H_4O_6$. Add **NH_4OH** in excess. $Ba_3(PO_4)_2$, $BaHPO_4$, etc.; and BaC_2O_4, will be precipitated. If there is no precipitate, these acids are absent. Special tests must now be applied to separate portions of the original solution or dry salt.

5. **H_3PO_4, Phosphates.**

If the solution is an aqueous one, add **"magnesia mixture."** A white ppt., on standing, indicates phosphates.

If the salt is soluble in acids only, dissolve a portion in **HNO_3**, and to this solution add an HNO_3 solution of **ammonium molybdate.** A yellow ppt., on heating solution to temperature not higher than 40°, indicates H_3PO_4.

Add **$NaC_2H_3O_2$**, make acid with **$HC_2H_3O_2$**, add **Fe_2Cl_6**, drop by drop, avoiding excess. Gelatinous, brownish-white ppt., $F_2(PO_4)_2$, indicates phosphates.

6. **$H_2C_2O_4$, Oxalates.**

Substance heated with **H_2SO_4** gives off CO_2 and CO.

Precipitate with $CaCl_2$ and add **$HC_2H_3O_2$**; if the ppt. formed is insoluble, an oxalate is present.

7. **H_3BO_3, Borates.**

Acidify with **HCl**, and moisten a piece of yellow **turmeric paper** with the solution. Dry the paper on a test tube of boiling water. A red tinge, changing to greenish black on moistening the dry paper with **Na_2CO_3**, indicates borates.

Cover salt with **alcohol** and add a little conc. **H_2SO_4**. Kindle alcohol. Greenish-yellow flame indicates borates.

8. **HF, Fluorides.**

Mix some of the dry powder with **H_2SO_4**, and heat in a platinum or lead crucible, covered with a glass plate. If glass is etched, fluorides are present.

9. **$H_2C_4H_4O_6$, Tartrates.**

Recognized in the preliminary examination by the blackening of the substance and the odor of burnt sugar.

Add **NaOH** and **$CaCl_2$**, filter off ppt., and add to it **NaOH.** Precipitate dissolves, but forms again on boiling.

6. $H_2C_2O_4$, Oxalates.

The solubility of the Ca salt in HCl and HNO_3 distinguishes oxalates from sulphates, while its insolubility in $HC_2H_3O_2$ acts as a distinction from tartrates. Certain oxalates, principally ferric and chromic, are not precipitated by $CaCl_2$, since they form soluble double salts. Fluorides may be mistaken for oxalates by this test; hence, if the former are found, another test for oxalates must be applied.

Reaction with H_2SO_4:

$$M_2C_2O_4 + H_2SO_4 = CO + CO_2 + H_2O + M_2SO_4.$$

In the case of free $H_2C_2O_4$, the H_2SO_4 merely removes the elements of water.

Reaction:

$$H_2C_2O_4 = CO + CO_2 + H_2O.$$

7. H_3BO_3, Borates.

For flame test, see Fresenius, par. 144, 6; Chemical Lecture Experiments, Newth, under Boron.

For turmeric test, see Fresenius, par. 144, 7.

8. HF, Fluorides.

Reaction with H_2SO_4:

$$2MF + H_2SO_4 = 2HF + M_2SO_4.$$

HF with glass:

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

(See Fresenius, par. 146, 5, 6, 7; par. 147.)

9. $H_2C_4H_4O_6$, Tartrates.

Reaction with $CaCl_2$:

$$M_2C_4H_4O_6 + CaCl_2 = CaC_4H_4O_6 + 2MCl.$$

TABLE XII.—ANALYSIS OF GROUP II.

HI, HBr, HCl, HCN, H_2S, $H_4Fe(CN)_6$, $H_3Fe(CN)_6$.

H_2S will have been discovered in the preliminary examination. If present, it must be expelled before testing for the other members of the Group. To a portion of the original solution, in which there is no H_2S, and from which acids of Group I have been removed, acidified with **HNO_3**, add **$AgNO_3$**. The silver salts of the members of this Group will be precipitated. Add **NH_4OH**; all dissolve out except AgI and $Ag_4Fe(CN)_6$. Separate portions of the original solution must be tested for each acid.

1. **HI, Iodides.**	2. **HBr, Bromides.**	3. **HCl, Chlorides.**	4. **HCN, Cyanides.**	5. **$H_4Fe(CN)_6$, Ferrocyanides.**	6. **$H_3Fe(CN)_6$, Ferricyanides.**
To a cold neutral, or slightly acid, solution, add a little thin **starch paste** and **Cl water.** The formation of a blue compound indicates iodides. **CS_2**, with the solution of an iodide and weak **Cl water,** is colored violet.	Heat a portion of the dry salt with **H_2SO_4** and **MnO_2**. Br vapors are given off, recognized by deep brown color. To discover HBr in presence of HI, **CS_2** is added, and then a weak solution of **Cl water.** Shake the tube, and the CS_2 will have a brown color if HBr alone is present, but violet, if HI is present. On further addition of Cl water, HI will disappear, and CS_2 will give the Br reactions.	Heat a portion of dry salt with **H_2SO_4** and **MnO_2**; Cl is given off, bleaching moistened litmus paper. To discover HCl in presence of HBr and HI, treat a portion of solution with conc. **H_2SO_4** and solid **$K_2Cr_2O_7$**. Distill, and collect distillate, CrO_2Cl_2 and Br. Add **NH_4OH.** Yellow solution, $(NH_4)_2CrO_4$, indicates HCl. Confirm by adding to this yellow solution **$Pb(C_2H_3O_2)_2$** and **$HC_2H_3O_2$**. Yellow $PbCrO_4$ will form.	HCN (poisonous), liberated by **H_2SO_4** from its compounds, is recognized by the odor of bitter almonds. To a portion of the original solution add **NaOH, $FeSO_4$,** few drops **Fe_2Cl_6,** and **HCl** in excess; a blue compound, $Fe_4(Fe(CN)_6)_3$, indicates presence of cyanides.	To a portion of the solution add **Fe_2Cl_6**; a deep blue precipitate shows the presence of ferrocyanides.	To a portion of the solution add **$FeSO_4$**; a deep blue precipitate indicates ferricyanides.

Explanation of Table XII.

The acids of this Group are distinguished from those of Group I by forming soluble Ba salts and insoluble Ag salts, while the Ba salts of Group I are all insoluble, and the Ag salts *nearly* all insoluble.

H_2S must be removed, as the black AgS would interfere with detection of the other acids. Free H_2S is expelled by boiling until the escaping fumes fail to blacken paper moistened with solution of $Pb(C_2H_3O_2)_2$. H_2S, in combination with alkali and alkaline earth metals (the only metals whose sulphides will pass into solution without decomposition), is precipitated by a salt which will not precipitate any of the other acids that may be present.

Of course, those acids of Group I which are precipitated by $AgNO_3$ must also be removed. Acidulation with HNO_3 prevents solution of Ag salts by alkalies.

The precipitated Ag salts are treated with NH_4OH, to separate HI from the rest of the Group. $Ag_4Fe(CN)_6$ is only sparingly soluble, and may be left with the insoluble AgI.

The members of this Group are all easily detected when present separately. When chlorides, bromides, and iodides are present together, their recognition is a matter of some difficulty.

1. **HI, Iodides.**

Both starch and CS_2 tests depend on the fact that Cl possesses a stronger affinity for the metals than I does. The I is consequently liberated. *Weak* Cl water must be used, and an excess avoided, lest the I be oxidized, destroying the color. (For starch compound, see Prescott, p. 265, note. See also American Journal of Science, June, 1894, Vol. XLVII., p. 422.)

2. **HBr, Bromides. Reaction for first test:**

$$2KBr + 2H_2SO_4 + MnO_2 = 2Br + K_2SO_4 + MnSO_4 + 2H_2O.$$

The detection of HBr in presence of HI depends on the fact that Cl will set free all of the I before any of the Br, and will, when added in excess, oxidize the liberated I to HIO_3, iodic acid. It is probable that chlorides of I are also formed. These compounds take away the color of free I from the CS_2. When the I has been entirely oxidized, the Br reaction will appear. (See Prescott, par. 920.)

3. **HCl, Chlorides.**

In absence of HBr and HI, a white precipitate with $AgNO_3$, dissolving at once in NH_4OH, is sufficiently distinctive.

The reaction with H_2SO_4 and MnO_2 is similar to that for HBr.

Reactions for HCl in presence of HBr and HI:

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 = 2CrO_2Cl_2 + 2Na_2SO_4 + K_2SO_4 + 3H_2O.$$

At the same time Br (free) distills over, and obscures color of "chloro-chromic anhydride." On addition of NH_4OH,

however, Br forms a colorless solution, while CrO_2Cl_2 gives ammonium chromate, with characteristic color of chromates. Acids change this color to the reddish-yellow of dichromates. $Pb(C_2H_3O_2)_2$ gives $PbCrO_4$:

$$CrO_2Cl_2 + 2NH_4OH = (NH_4)_2CrO_4 + 2HCl.$$
$$(NH_4)_2CrO_4 + Pb(C_2H_3O_2)_2 = PbCrO_4 + 2NH_4C_2H_3O_2.$$

4. **HCN, Cyanides. Reactions:**

$$FeSO_4 + Fe_2Cl_6 + 8NaOH = Fe_2(OH)_6 + Fe(OH)_2 + Na_2SO_4 + 6NaCl.$$
$$2Fe_2(OH)_6 + 3Fe(OH)_2 + 18KCN = Fe_4(Fe(CN)_6)_3 + 9K_2O + 9H_2O.$$
$$Fe_2(OH)_6 + Fe(OH)_2 + 8HCl = Fe_2Cl_6 + FeCl_2 + 8H_2O.$$

5. **$H_4Fe(CN)_6$, Ferrocyanides. Reaction:**

$$3K_4Fe(CN)_6 + 2Fe_2Cl_6 = Fe_4(Fe(CN)_6)_3 + 12KCl.$$

6. **$H_3Fe(CN)_6$, Ferricyanides. Reaction:**

$$2K_3Fe(CN)_6 + 3FeSO_4 = Fe_3(Fe(CN)_6)_2 + 3K_2SO_4.$$

(See Roscoe and Schorlemmer, Vol. II., Part II., p. 105 *sq.*)

TABLE XIII.—ANALYSIS OF GROUP III.

HNO_3, $HClO_3$, $HC_2H_3O_2$.

The preliminary examination will have given the analyst evidence of these acids.

1. **HNO_3, Nitrates.**	2. **$HClO_3$, Chlorates.**	3. **$HC_2H_3O_2$, Acetates.**
Pour into the solution an equal amount of a concentrated solution of **$FeSO_4$**. Add strong **H_2SO_4** in the cold, pouring it down the side of the test tube, not allowing it to mix; a brown or black ring between the two liquids indicates nitrates. Add **H_2SO_4** and a bit of **Cu**. Reddish-brown fumes are liberated. If iodides or bromides be present, they must be removed with **$HgCl_2$**, as they also give a dark coloration from decomposition with H_2SO_4.	Pour upon the dry salt **HCl** or **H_2SO_4**; a yellow coloration, with the emission of yellowish-green gas, bleaching a solution of indigo, indicates chlorates.	To a portion of the solution, rendered strictly neutral, add a few drops of **Fe_2Cl_6**; a red coloration, caused by the formation of $Fe_2(C_2H_3O_2)_6$, indicates acetates. On boiling, a brown basic salt should form, leaving the solution colorless. Before applying this test, phosphoric and oxalic acids must be removed.

Explanation of Table XIII.

1. HNO_3, Nitrates.

H_2SO_4 decomposes the nitrate, liberating HNO_3. This is reduced by the $FeSO_4$, and NO is disengaged. This combines with the $FeSO_4$, forming a purple or dark-brown liquid. As this liquid is decomposed by heat, care must be taken to allow everything to cool. Some of the $FeSO_4$ is oxidized; hence it must be in excess, so as to leave some to combine with the NO.

Reactions:

$$2KNO_3 + 4H_2SO_4 + 6FeSO_4 = 2NO + 3Fe_2(SO_4)_3 + K_2SO_4 + 4H_2O.$$

$$NO + 2FeSO_4 = (FeSO_4)_2NO.$$

In the second test, Cu is used to decompose the liberated HNO_3. A crystal of $FeSO_4$ acts in the same way.

Reactions:

$$2KNO_3 + 4H_2SO_4 + 3Cu = 2NO + 3CuSO_4 + K_2SO_4 + 4H_2O.$$

$$NO + O = NO_2.$$

2. $HClO_3$, Chlorates.

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + H_2O + Cl_2O_4.$$

$$2Cl_2O_4 = Cl_2O_3 + Cl_2O_5.$$

The bleaching of indigo is due to liberation of Cl or its lower oxides.

Extreme care must be taken in this test. Heat must be avoided, and very small quantities used, as there is danger of violent explosion.

3. $HC_2H_3O_2$, Acetates.

Reactions:

$$6NaC_2H_3O_2 + Fe_2Cl_6 = Fe_2(C_2H_3O_2)_6 + 6NaCl.$$

$$Fe_2(C_2H_3O_2)_6 + 2H_2O = Fe_2(C_2H_3O_2)_4(OH)_2 + 2HC_2H_3O_2.$$

The solution must be strictly neutral, because alkalies precipitate the base from reagent, and acids discolor the $Fe_2(C_2H_3O_2)_6$ solution. The last reaction serves to distinguish acetates from thiocyanates.

PART III.—PRELIMINARY EXAMINATION.

THE analyst must take care not to place too much value upon the results of the Preliminary Examination, as in most cases great probability of the presence of substances is all that can be arrived at.

If the substance is a liquid, a portion of it must be evaporated to see if it is entirely volatile or leaves a residue. If volatile, it may be pure water, an acid, or some organic liquid, such as alcohol, ether, etc. If a residue remains, it must be treated according to the methods given below for solids.

If the substance is a solid, and neither a metal nor an alloy, a portion must be powdered in a clean porcelain or steel mortar, and parts of this portion treated in each of the following ways:

1. Heat in a bulb tube. (Consult Table XIV.)
2. Heat on charcoal in the blowpipe flame. (Consult Table XV.)
3. Fuse in the borax bead. (Consult Table XVI., 1.)
4. Treat with concentrated H_2SO_4. (Consult Table XVI., 2.)
5. Heat in the Bunsen flame, and note colorations of flame. (Consult Table XVI., 3.)

TABLE XIV.—REACTIONS IN BULB TUBE.

Heat a small portion of the dry substance in a dry, clean, bulb tube, observing changes of color in the substance, properties of sublimates and of escaping gases. If no change is effected, even at a very high temperature, organic matter is absent, as also salts containing water of crystallization, readily fusible substances, volatile bodies, and those which change color.

1. **Changes of Color:**
   - Substance blackens, with separation of C; burnt odor, gases escape—organic substances. (Fresenius, par. 176, g.)
   - Substance blackens, without evidence of carbonization — certain compounds of Ni, Co, or Cu.
   - Yellow hot, white cold—ZnO and Zn salts.
   - Yellow hot, yellow cold—PbO and Pb salts. Substance fuses at red heat.
   - Orange up to reddish-brown hot, pale yellow cold—Bi_2O_3 and Bi salts.
   - Brownish-red up to black hot, brownish-red cold—Fe_2O_3.
   - Brown hot, brown cold—$Cd(OH)_2$ and many Cd salts.
   - Brown hot, dirty yellow cold—SnO_2.

2. **Gases Escape:**
   - SO_2—odor of burning S, bleaches litmus—sulphites, thiosulphates, some sulphates.
   - CN—odor of bitter almonds, "peach blossom" flame—cyanides.
   - NH_3—pungent odor, alkaline reaction — decomposable NH_4 compound.
   - O—enkindles glowing taper — peroxides (some monoxides, as HgO), chlorates, nitrates, etc.
   - H_2S — blackens "Pb paper" — hydrated sulphides.
   - NO_2—reddish-brown, acrid vapors—nitrates or nitrites.
   - $(CH_3)_2CO$—acetone, fragrant odor—acetates.

3. **Sublimates:**
   - Red-brown drops, solidifying to yellow—S, free or from sulphides.
   - Black, violet vapor—I.
   - White crystalline—NH_4 compounds, not decomposed by heat; viz., haloid salts and carbonate.
   - White crystalline; small, shiny octahedrons—As_2O_3.
   - White crystalline; thick, irritating fumes—$H_2C_2O_4$.
   - White crystalline needles, after substance fuses to yellow liquid—Sb_2O_3.
   - White crystalline after fusing—$HgCl_2$.
   - White, yellow hot, without previous fusion—Hg_2Cl_2.
   - Yellow, red on rubbing—HgI_2.
   - Black, red on rubbing—HgS.
   - Gray, rubbing to silvery globules—Hg.
   - Steel-gray mirror, garlic odor—As.

TABLE XV.—REACTIONS ON CHARCOAL.

1. **On Charcoal Alone** (blowpipe flame):
   - Decrepitation—salts containing water.
   - Deflagration—nitrates, chlorates, etc.
   - SO_2 given off—S and compounds, usually sulphides.
   - Substance fuses and is absorbed by the charcoal—salts of Group I and some of Group II.
   - Substance is infusible and incandescent:
     - BaO, SrO, CaO, MgO—residue alkaline.
     - Al_2O_3, ZnO (yellow hot), SiO_2—residue not alkaline.
     - Treat as in 2.
   - An incrustation forms on the charcoal. Treat as in 3.

2. **On Charcoal with $Co(NO_3)_2$** (outer blowpipe flame):
   - Blue coloration—Al.
   - Yellowish-green—ZnO.
   - Flesh color or pink—MgO.
   - Bluish-green—SnO.
   - Brick-red—BaO.
   - Gray—SrO, CaO.
   - Dirty dark green—Sb_2O_3.
   - Slight blue indicates phosphates of Ba, Sr, Ca, Mg, in presence of SiO_2.

3. **On Charcoal with Na_2CO_3** (inner blowpipe flame):

   Mix with equal amount of Na_2CO_3.

GLOBULE.	INCRUSTATION. HOT.	COLD.	
Brittle, . .	White, ...	White, ...	Sb.
" . .	Dark orange,	Lemon yel'w,	Bi.
Malleable,	Lemon yel'w,	Bright "	Pb.
"	Dark red, . .	—————	Ag.
Red Malleable, . .	no incrustation, . .		Cu.
———, . .	Yellow, . . .	White, ...	Zn.
———, . .	Red-brown, .	Red-brown, .	Co.
———, . .	———, . . .	White, ...	As.

   - Scattered globules may be cut out and fused into one.
   - Fe, Ni, and Co give dark magnetic powder.

TABLE XVI.—REACTIONS WITH $Na_2B_4O_7$, H_2SO_4, AND BUNSEN FLAME.

1. Fuse a very small quantity in borax bead in both blowpipe flames:

	OUTER FLAME.	INNER FLAME.
Cu	Blue,	Red or colorless.
Co	Blue,	Blue.
Ni	Reddish-brown,	Gray or colorless.
Fe	Colorless to yel'w,	Bottle green.
Mn	Amethyst,	Colorless.
Cr	Yellowish-green,	Emerald green.
Ba, Sr,	Colorless,	Enamel white.

2. Cover a small quantity of dry substance with concentrated H_2SO_4, and heat moderately, not high enough to vaporize the H_2SO_4:

Cl_2O_4—greenish-yellow, acrid odor—chlorates. (Discontinue heat.)

I—violet vapor—iodides. HI, H_2S, SO_2 are also given off.

Br—brown vapor, acrid odor—bromides. HBr and SO_2 are also given off.

NO_2—reddish-brown gas, pungent odor—nitrates or nitrites.

SO_2—odor of burning S, bleaches litmus—sulphites.

SO_2—with precipitation of S—thiosulphates.

CO—burning with blue flame—oxalates.

CO_2—sudden effervescence, renders lime water turbid—carbonates or oxalates.

HCl—forms heavy white cloud with NH_3, or renders turbid AgCl. HNO_3 also gives a white cloud with NH_3. CO_2 may also render $AgNO_3$ turbid.

3. **Flame Colorations.**

Ignite a small portion on platinum wire in the colorless Bunsen flame:

Violet	coloration,	K.
Carmine	"	Li.
Crimson	"	Sr.
Yellowish-red	"	Ca.
Yellow	"	Na.
Yellowish-green	"	Ba.
Bright green	"	Cu.
Light green	"	H_3BO_3.
Pale blue	"	Pb or As.

PART IV.—SOLUTION OF SOLID SUBSTANCES. SPECIAL TREATMENT OF INSOLUBLE SUBSTANCES, AND OF METALS AND ALLOYS.

1. **Treatment with Water.**
2. **Treatment with Acids.**
3. **Treatment of Substances Insoluble in Water and Acids.**
4. **Treatment of Metals and Alloys.**

1. **Treatment with Water.**—A portion of the substance is powdered, and first treated with cold water, and then boiled. A few drops of the clear liquid obtained by filtering are evaporated on a piece of clean platinum foil. Should a residue remain on the foil, the substance must be treated with water until nothing remains after evaporation. The results of the several treatments are put together and reserved for the regular course of analysis as in Part I. Should the liquid become turbid, but clear up on adding a few drops of HCl or HNO_3, Bi or Sb may be present.

2. **Treatment with Acids.**—If the substance does not dissolve entirely in water, the residue is washed, and boiled, first with dilute HCl, and then with strong HCl, testing on the platinum foil each time to see if anything has dissolved. Should there still be something undissolved, it must be washed and treated with dilute HNO_3, and then with strong HNO_3, testing each treatment on the foil as before. If the substance still remains partly or entirely unacted upon, it is to be treated with aqua regia. If it still resists, the residue must be well washed and treated as in Table XVII. Should anything dissolve in any one of the treatments with acids, it must be reserved for analysis by Part I.

All these different solutions must be analyzed separately.

TABLE XVII.

3. Treatment of Substances Insoluble in Water and Acids.

To this class belong $BaSO_4$, $SrSO_4$, ($CaSO_4$), $PbSO_4$; AgCl, AgBr, AgI; AgCN, $Ag_4Fe(CN)_6$, $Ag_3Fe(CN)_6$; SiO_2, and many silicates; native and ignited Al_2O_3; ignited Cr_2O_3; chrome iron ore; CaF_2, and other fluorides not decomposed by acids, S and C.

Part I.—Boil the substance several times with $NH_4C_2H_3O_2$, and filter.

Solution.—Divide into two parts.

(A) Add **H_2SO_4**; white ppt., $PbSO_4$, indicates Pb.

(B) Add **$BaCl_2$**; white ppt., $BaSO_4$, insoluble in dilute **HCl**, indicates sulphuric acid.

Residue may contain any of the above substances except Pb. Add **KCN**, and, if S has not been detected, boil.

Solution.—Add **$(NH_4)_2S$**; brownish-black ppt., Ag_2S, indicates Ag. Confirm by filtering off the ppt., dissolving it in **HNO_3**, and adding to the solution **HCl**; white ppt., AgCl, indicates Ag.

Residue may contain any of the above salts except those of Pb and Ag. If S is present, it must be expelled by long ignition in a covered porcelain crucible over the blowpipe. Mix with 2 parts **Na_2CO_3**, 2 parts **K_2CO_3**, and 1 part **KNO_3**, heat in a platinum crucible to quiet fusion, cool suddenly, remove fused mass, boil with water, and filter.

Solution.—Divide into two parts:

(A) Acidify with **$HC_2H_3O_2$**, and add **$Pb(C_2H_3O_2)_2$**; yellow ppt., $PbCrO_4$, indicates Cr.

(B) Evaporate to dryness with a few drops of **HCl**, dissolve residue in **H_2O**; a gritty powder remaining indicates SiO_2. Filter, and divide the filtrate into two parts.

(1) Add **HNO_3** and **NH_4OH**; white ppt., $Al_2(OH)_6$—Al.

(2) Test for acids.

Residue contains the bases as carbonates. Add **HCl**, evaporate to dryness, and dissolve in **H_2O**. Filter off any gritty powder, SiO_2, and submit the solution to regular course of basic analysis.

Part II.—If Ag is present, take a portion of the original substance and treat with **hot water**, then with dil. **HNO_3**, and filter. Boil the residue in **NaOH**.

Solution.—Acidify with **HCl**, and test for ferrocyanic and ferricyanic acid.

Residue.—Wash, treat with **Zn**, **H_2O**, and **H_2SO_4** for about ten minutes. Filter, test filtrate for HCl, HBr, HI, and HCN.

Part III.—If K and Na are to be sought for in combined silicates, a portion of the substance must be heated, with 8 parts precipitated **$CaCO_3$** and 1 part **NH_4Cl**, in a platinum crucible for half an hour. The crucible and contents are put in a beaker with water, and heated for some time to a temperature near the boiling point. Filter, and treat the filtrate with **NH_4OH** and **$(NH_4)_2CO_3$** to remove Ca salts. Filter, evaporate filtrate, and expel NH_4 salts by ignition; test the residue for K, Na, and Li.

S and C will have been recognized in the preliminary examination.

4. Treatment of Metals and Alloys.

The alloy is powdered, or beaten out into a thin sheet, if possible, and then treated with hot HNO_3. From the action of HNO_3 on the metals, they are divided into three classes:

1. Those which dissolve in HNO_3.
2. Those which do not dissolve, but which form oxides insoluble in water and in HNO_3.
3. Those which are not acted upon by HNO_3.

1. To the first class belong all metals except Sb, Sn, Au, and Pt. If the substance dissolves entirely, the solution is evaporated to dryness, and the residue dissolved in $H_2\bar{O}$, with the aid of a little HNO_3 if necessary. If an oxide forms, it is filtered off, and the filtrate tested on platinum foil to ascertain whether it contains anything, then filtered, the filtrate is evaporated, and the residue taken up with water. The solution in water is examined for bases according to the Tables of Basic Analysis.

2. Should an oxide form, it must be filtered off, washed, and dissolved in HCl. The solution is tested for Sb and Sn.

3. To the third class belong Au and Pt. Should the metal or alloy resist the action of HNO_3, it must be treated with aqua regia. The solution is divided into two parts. To the first portion a mixture of $SnCl_2$ and Fe_2Cl_6 is cautiously added; a fine precipitate of a purple color indicates Au.

To the second portion NH_4Cl is added; a yellow precipitate, $(NH_4)_2\ PtCl_6$, indicates Pt.

TABLE XVIII.—SOLUBILITIES.

1 = soluble in water; 2 = soluble in acids only; 3 = insoluble in water and acids; 4 = sparingly soluble in water and acids; 5 = sparingly soluble in water, soluble in acids; 6 = sparingly soluble in acids, insoluble in water.

	Acetate.	Arseniate.	Arsenite.	Borate.	Bromide.	Carbonate.	Chlorate.	Chloride.	Chromate.	Cyanide.	Ferricyanide.	Ferrocyanide.	Fluoride.	Hydroxide.	Iodide.	Nitrate.	Oxalate.	Oxide.	Phosphate.	Silicate.	Sulphate.	Sulphide.	Tartrate.	
Aluminium . .	1	2	–	2	1	2	1	1	–	–	–	–	1	2	1	1	2	6 & 3	2	6	1	2	1	Aluminium.
Ammonium . .	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	Ammonium.
Antimony . . .	–	2	2	–	5	–	–	5	2	–	–	–	1	2	5	–	2	2	5	–	2	2	*1	Antimony.
Barium	1	2	2	2	1	2	1	1	2	5	–	5	6	1	1	1	2	1	5	2	3	1	2	Barium.
Bismuth . . .	1	2	–	2	5	2	1	5	2	–	–	–	1	2	2	1	2	2	2	–	1	2	2	Bismuth.
Cadmium . . .	1	2	–	5	1	2	1	1	2	2	–	–	5	2	1	1	2	2	2	2	1	2	5	Cadmium.
Calcium . . .	1	2	2	2	1	2	1	1	5	1	1	1	2	5	1	1	2	5	5	2	4	5	2	Calcium.
Chromium . . .	1	2	–	2	4	2	1	4	2	2	–	–	1	2	1	1	5	6 & 3	2	2	5	6	1	Chromium.
Cobalt	1	2	2	2	1	2	1	1	2	6	3	3	5	2	1	1	2	2	2	2	1	2	1	Cobalt.
Copper	1	2	2	2	1	2	1	1	1	2	–	3	2	2	1	1	2	2	2	2	1	2	1	Copper.
Ferric comp. .	1	2	2	2	1	2	1	1	1	–	1	3	1	2	1	1	2	2	2	2	1	2	1	Ferric comp.
Ferrous comp.	1	2	2	2	1	2	1	1	–	6	3	3	5	2	1	1	2	2	2	2	1	2	5	Ferrous comp.
Lead	1	2	2	2	4	2	1	4	6	2	5	2	2	2	5	1	2	2	2	2	6	2	2	Lead.
Magnesium . .	1	2	2	5	1	2	1	1	1	1	1	1	6	2	1	1	2	2	2	2	1	2	5	Magnesium.
Manganese . .	1	2	2	2	1	2	1	1	1	2	3	2	2	2	1	1	5	2	2	2	1	2	5	Manganese.
Mercurous comp.	5	2	2	–	6	2	1	6	2	–	–	–	–	–	2	1	2	2	2	–	5	2	5	Mercurous comp.
Mercuric comp. .	1	2	2	–	1	2	1	1	5	1	–	–	5	–	2	1	2	2	2	–	1	2	2	Mercuric comp.
Nickel	1	2	2	2	1	2	1	1	2	6	3	3	5	2	1	1	2	2	2	2	1	2	2	Nickel.
Potassium . . .	1	1	1	1	1	1	1	1	1	1	1	1	1	6	1	1	1	1	1	1	1	1	1	Potassium.
Silver	1	2	2	2	2	2	1	3	2	3	3	3	1	–	3	1	2	2	2	–	5	2	2	Silver.
Sodium	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	Sodium.
Strontium . . .	1	2	2	2	1	2	1	1	5	1	–	1	6	1	1	1	2	1	2	2	3	1	2	Strontium.
Stannous comp. .	1	2	2	2	–	–	1	1	2	–	–	–	1	2	1	–	2	2	2	–	1	2	2	Stannous comp.
Stannic comp. .	1	2	–	–	–	–	–	1	–	–	–	–	1	2	1	–	1	6	2	–	–	2	–	Stannic comp.
Zinc	1	–	–	2	1	2	1	1	1	2	2	6	5	2	1	1	2	2	2	2	1	2	2	Zinc.

* Potassium antimonyl tartrate, "tartar emetic," soluble in water.

APPENDIX.

REAGENTS.

Acids :

HCl dilute: 4 parts of water to 1 of acid.
HNO_3 " 3 " 1 "
H_2SO_4 " 5 " 1 "
$HC_2H_3O_2$: 30 per cent. acid; Sp. Gr. 1.04.

Ammonium Carbonate, $(NH_4)_2CO_3$. Dissolve one part by weight in four parts of water, after which one part of reagent NH_4OH is added, to prevent change to NH_4HCO_3.

Ammonium Chloride, NH_4Cl. One part of crystallized salt in eight parts of water.

Ammonium Hydroxide, NH_4OH. Commercial aqua ammonia is generally stronger than required for reagent. Reagent strength is 10 per cent. of NH_3 gas; Sp. Gr. .96. Reduce to required strength.

Ammonium Molybdate, $(NH_4)_2MoO_4$. Dissolve 60 grams in 400 cc. of reagent, NH_4OH; then add 400 cc. of distilled water; then cautiously add 500 cc. of nitric acid, Sp. Gr. 1.4.

Ammonium Oxalate, $(NH_4)_2C_2O_4$. Dissolve one part of crystallized salt in twenty-four parts of water.

Ammonium Sulphide, $(NH_4)_2S$. Purchased ready for use; or may be made by passing H_2S into reagent ammonia till solution no longer precipitates $MgSO_4$. Changes on standing to the yellow sulphide.

Barium Chloride, $BaCl_2$. One part of crystallized salt in ten parts of water.

Calcium Chloride, $CaCl_2$. One part of crystallized salt in eight parts of water.

Calcium Hydroxide, $Ca(OH)_2$, limewater. Agitate slaked lime in water, and allow to settle. Decant the clear liquid and keep stoppered.

Calcium Sulphate, $CaSO_4$. Saturated solution.

Cobalt Nitrate, $Co(NO_3)_2$. One part in ten parts of water.

Ferric Chloride, Fe_2Cl_6. One part in fifteen parts of water.

Lead Acetate, $Pb(C_2H_3O_2)_2$. One part in ten parts of water.

" Magnesia Mixture." Dissolve one part of crystallized $MgSO_4$ and two parts of pure NH_4Cl in eight parts of water; then add four parts reagent NH_4OH, let stand, and filter.

Magnesium Sulphate, $MgSO_4$. One part in ten parts of water.
Mercuric Chloride, $HgCl_2$. One part in sixteen parts of water.
Nessler's Reagent. As in Shepard.
Potassium Dichromate, $K_2Cr_2O_7$. One part in ten parts of water.
Potassium Ferricyanide, $K_3Fe(CN)_6$. One part in twelve parts of water.
Potassium Ferrocyanide, $K_4Fe(CN)_6$. One part in twelve parts of water.
Potassium Iodide, KI. One part in twenty parts of water.
Potassium Sulphocyanide, KSCN. One part in twenty-five parts of water.
Silver Nitrate, $AgNO_3$. One part in fifty parts of water.
Sodium Phosphate, Na_2HPO_4. One part in ten parts of water.
Sodium Hydroxide, NaOH. One part in nine parts of water.
The other reagents are used dry.

NOTE.—For list of impurities, see "Elements of Chemistry," Shepard, pp. 351 *sq.*